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Optimizing the sintering of Cr2O3-nano powders for HVOF applications.

PROYECTO FIN DE CARRERA

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Realizado el acto de defensa y lectura del Proyecto Fin de Carrera el día __ de _____ de 20__ en Leganés, en la Escuela Politécnica Superior de la Universidad Carlos III de Madrid, acuerda otorgarle la CALIFICACIÓN de

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Abstract

The main focus on the project is tailoring a new ceramic coating material, Cr_2O_3 with the optimum combination of both good mechanical and corrosion resistance properties.

With several combinations with the amount of additive (%YSZ) mixed with the main powder Cr_2O_3, and applying two different atmospheres (H_2 and Ar-6%N_2) and a number of sintering temperatures we will achieve a space of possible candidates from where it will be chosen the optimum parameters which ultimate properties will reach the highest values.

After applying different conditions in a bunch of twenty samples two tests will be developed. An agglomeration strength test is necessary to obtain breaking points out of compressive tests on nanopowders and a study on grain growth is mandatory to control the enlargement of the powders after sintering.

Numeric values of breaking points and over 300 SEM pictures they will all contribute to decide about the best parameters for the coating to complete the most favourable settings to be able to spray effectively Cr_2O_3 nanopowders with HVOF.

Preface

- **Background**

This thesis study is a part of the project HIPECO2 (High Performance Ceramic Coatings for Extreme Conditions 2) based on the development of a new way to perform nano-powders of ceramic to be able to be sprayed properly with the thermal spray process HVOF (High Velocity Oxy Fuel). The research project is an agreement between Universidad Carlos III de Madrid and Technical Research Center of Finland (VTT) in collaboration with Helsinki University of Technology (HUT) and THE National Technology Agency of Finland (TEKES) among various Finnish industrial partners.

- **The goal of the thesis**

HIPECO 2

The High Performance Ceramic Coatings for Extreme conditions (HIPECO2) is a project based on tailoring ceramic coating materials with the optimum combination of good mechanical and corrosion properties. A new form to design thermal spray coatings is developed by mixing good parameters as minimizing the particle size and improving the strength of the agglomerates. The main goal is developing a new material compositions and structures to obtain zero porosity, high fracture toughness and good corrosion resistance in coating.

By combining the development of this new material system and the manufacturing of the powder with those characteristics we expect net technological discoveries to be used in conventional coating technologies in industrial scale. Therefore creating the new nano-fraction ceramic composite structure for the demanding applications, the new breakthrough will be suitable for further applications with improved properties.

Corrosion tests for coatings, anti-fouling properties, insulation and strengtheners and/or possible stabilizers are the main objectives to achieve after the core development of the optimum parameters for an industrial scale of thermal spray processes.

Motivation and Objectives

The aim of this Master Thesis was to develop new ceramic coating material to be able to be effectively sprayed with HVOF (High Velocity Oxy-Fuel) with the optimum parameters to achieve a subsequent good mechanical and corrosion resistance properties in extreme conditions. The objectives to obtain those parameters are based on improving particle strength, controlling the grain growth and therefore optimizing the atmosphere characteristics.

The project has to reach several goals; among the combination nanostructured granules, one of them should be remain granules in a solid state during HVOF process. This objective will be attained considering the composition, and selecting raw materials with higher melting point compared with the other components during the spray process.

In this work Cr_20_3 and different mixtures of Cr_2O_3-YSZ have been considered. To attain the aim of the project, the proposed materials have been sintered, then optimized the spray parameters and eventually the obtained HVOF coatings, have been characterized.

One of the challenges was to create a strength powder tests to take out all the pressure values where all the breakpoints are located. These results will tell us which is the pressure in every single analyzed sample where the agglomerates break in 1100, 1200, 1300°C temperatures and unsintered samples as well. Measurements have been done in a Universal Tensile Strength Machine (MTS 810).

Since a suitable size distribution of ceramic particles for HVOF technique is needed with many SEM pictures, taken after the sintering, it is determinate the grain growth of each sample under different sintering conditions of the atmosphere (as known 1100, 1200, 1300°C temperatures) and unsintered with multiple magnifications in all samples. A suitable size distribution for High-Velocity-Oxy-Fuel technique is needed.

The results from analyzing the grain growth and the agglomerate strengths will provide us the optimum sintering conditions to develop the powder.

1. Introduction

1.1 Processing of Modern Ceramics

Most ceramic fabrication processes begin with finely ground powder. Oxides such as alumina (Al_2O_3), magnesia (MgO) and zirconia (ZrO_2) occur naturally, but have to be purified by chemical processing before use as engineering ceramics.

An organic binder is usually present in order that the casting has sufficient strength to permit its removal from the mould before the firing operation. Plastic forming is possible if sufficient (25 to 50 %vol) organic additive is present to achieve adequate plasticity.

Efficient sintering is, therefore, promoted by the use of precursor powders of fine particle size. The diffusion process requires the presence of lattice vacancies and ceramics of covalent bonding have very high formation energy for vacancies and, therefore, exhibit low solid state diffusion rates, giving poor densification properties. Atom transport is predominantly by grain boundary diffusion so, again, a fine grain-size is essential for efficient densification.

In most cases, a '*densification aid*' or grain growth inhibitor is added to the ceramic to achieve maximum density and minimum grain size. The additives segregate to the newly-formed grain boundaries during sintering and increase the diffusion coefficient by forming low melting-point or low viscosity glass phase.[1]

1.2 Coatings; Properties and Characteristics:

Coatings are developed to be a solution against wear, corrosion, thermal degradation and other surface phenomena. Coating processes have to be compatible with physical substrate constraints as temperature and geometry. Thermal Spray can be customized to provide many requirements needed by the conditions of the susbtrates.

Overall, coatings structures can be categorised for thin films with atomic-scale deposition and thick coatings. Atomic deposition methods involve depositions of coating elements in atoms or clusters of atoms or molecules.

The principle of kinetic deposition is that the coating elements are introduced onto de substrate by admitting them kinetic energy.

A ceramic coating is a nonmetallic, inorganic coating made of sprayed aluminum oxide or of zirconium oxide, or a cemented coating of an intermetallic compound of essentially crystalline nature, applied as a protective film on metal to protect against temperatures above 1100°C.

The oxides of different metals are commonly called ceramics. The most used coatings are Aluminium Oxide (Al_2O_3), Chromium Oxide (Cr_2O_3), Titanium Oxide (TiO_2) and Zirconium Oxide (ZrO_2). They differ concerning temperature resistance, electric conductivity, acids and alkalis resistance.[2]

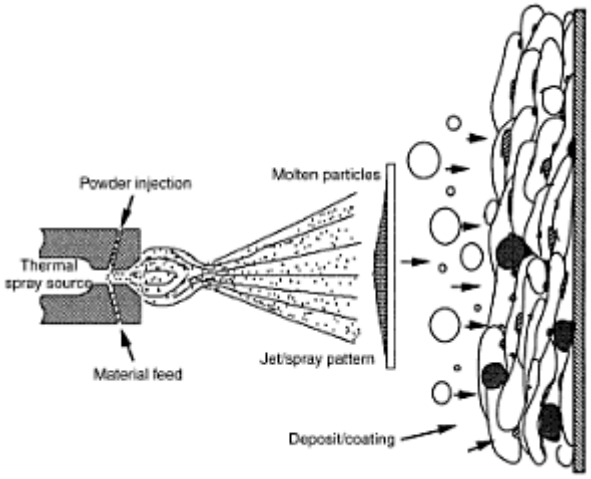


Figure 1.1: Typical thermal Spray Process and Coating

Figure 1.1.shows the main aspects of the process and how the particles impact a prepared surface and build up a lamellar structure characteristic of thermal spray process.

(i) Thermal Spray Coatings

Thermal Spray processes are nonatomistic, they don't deposit material onto surfaces as individual particles as atoms or molecules. The material instead is deposited in the form of liquid or semimolten particles on top of the surface. Coating feedstock material usually come in the form of powders, wires or rods and generally heated to their melting point and atomized and propelled toward the substrate by process gases or atomizing jets formed through nozzles.

Thermal spray can be also called "line-far-sighted" process due the projected stream of droplets deposits only onto surfaces that are directly in line with the spray stream.

Thermal spray processes are also characterized by having high coating rates due its high enthalpy and they are capable of operating over a broad range of temperature, velocity, and atmospheric conditions, enabling them to apply the greatest variety of materials.

Other advantages of thermal spray processes include a simplified waste-disposal stream and the ability to deposit thick coating sections.

Thermal spray coatings are considered to be "overlay" coatings, which can be defined as materials added to an original surface where there is little or no mixing or dilution between the coating and that substrate, thus preserving the composition of the base material. Some forces of the surface treatments are entirely diffusional in nature. IN these surface treatments, elemental materials are added to a base material through diffusional processes, which occur below the susbtrate surface and cause thickness build-up. Allowing may occur with the base materials to form new protective compounds or phases.

Diffusion and allowing often occur with thermal spray coatings, but the reaction zone is extremely narrow due to the extremely rapid cooling rates of the individual molten droplets impacting the relatively massive and cold substrate.

(ii) Coating Structures, Properties and Materials:

The main characteristics about coated surfaces are the combination among lamellar or layered splat structure, physical state of the droplets, pores, oxide inclusions, grains, phases, cracks and bond interfaces.

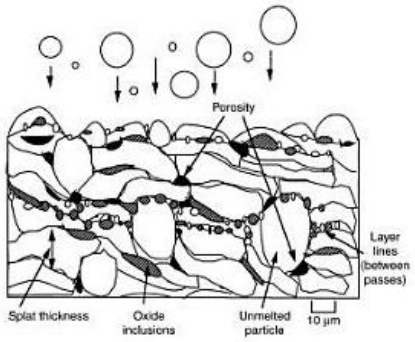


Figure 1.2. Thermal Spray Coating Microstructure showing common features.

- **Splat**:

Splat is the name given to every single droplet/particle when impacted. When many splats are deposited onto the substrate surface they overlap among them, then solidify and form a continuous coating layer. Splats are created when the particles are accelerated and impact a surface already prepared. The droplets are usually spherical and they become deformed when hitting the surface and

spread over it. Splats start stretching over the surface and at the same moment they fill the gaps and interstices spaces that are been formed on it. Figure 1.3.shows particles with its characteristic lamellar structure of the thermal spray coating.

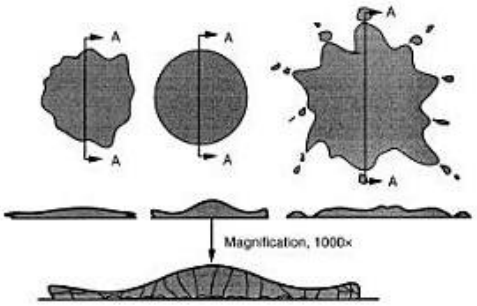


Figure 1.3. Typical Thermal Spray Splat for structures

Thermal spray processes are also characterized for its fast solidification. When the particles impact onto the surface, the heat is released quickly. The rapid cooling rates produce a wide range of material states, form amorphous to metastable.

- **Oxide Stringers:**

Oxide stringers are oxide inclusions than appear in metallic coatings and are visualized as dark strings, parallel to the substrate. Those oxide inclusion can be developed by interaction particle-atmosphere or heating of the coating surface during deposition. Contact of the hot particles with the surrounding environment develops oxide and/or nitride films on particle surfaces. Also long dwell times produce a rise of the thickness of the oxide or nitride films, leading higher concentrations of oxide on the substrate.

Generally, oxide inclusions add hardness to the whole hardness coating (Figure 1.4). So the combination of the metallic coating plus the oxide inclusions becomes harder than the metal coating itself. This makes the material more brittle as oxides fracture easily.

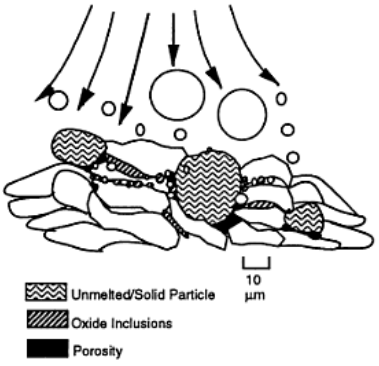


Figure 1.4 - Typical Thermal Spray Coating Effects

- **Porosity**:

Porosity is the most influential consequence in thermal spray processes. It modifies coating properties and it sometimes can be advisable. Porosity generates poor coating cohesion and leads to higher corrosion and wear rates. Porous are related to unmelted or resolidified particles stuck in the coating. Poor particle cohesion causes premature cracking, delamination or spalling. When the porous are open that enable possible corroding and oxidizing elements to attack the surface. Porosity also decreases the coating hardness and contributes to poor surface finishes, therefore porosity lowers wear resistance. On the other hand porosity may cause coating fragments that come off and become abrasive cutting agents which improve coating wear rates.

Sometime surfaces about to get coating have to be prepared beforehand. Machining or grinding are frequently methods to get the surface ready for spraying.

The sources of coating porosity are generally originated by

- Material shrinkage
- Entrapped unmelted, partially melted or resolidified particle
- Poor particle cohesion
- Intersplat or intrasplat cracking
- Porosity inherent to the feedstock

Those are some of the many reasons why we could get porosity onto the coated surface and the most common one is trapped, unmelted or resolidified particles.

1.3 Thermal Spray

Thermal Spray technique is method which includes all the coating processes used to apply metallic and non-metallic (composite and polymeric) materials sprayed towards the surface of any susbstrate. Finely divided droplets, in a molten or semimolten state, are accelerated by gases or atomization jets. A thermal energy generated by chemical (combustion) or electrical (plasma, arc…) is used to melt, semi melt and accelerate those particles among 50 to >1000m/s.

The raw materials are introduced into the thermal spray gun in form of wire, rod or powder so the energy source can heat up the materials. The particles propelled hit the surface and solidify once there, the solid drops start to overlap among them and join the surface of the substract forming a bond. The new surface built by the droplets begins to form a layer called “splat”, which are thin

layers or l*amellae* that conform and adhere to the substrate surface, and they will get as thicker as it needs.

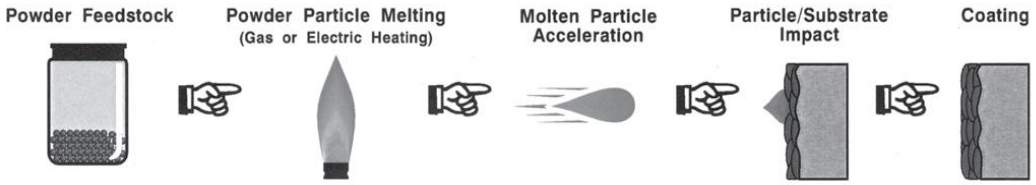


Figure 1.5: ***Thermal Spray Coating Process (Source: Graphic from International Thermal Spray Association)***

There are many different variables on which the layer structure will take form such as sprayed and substrate material, substrate temperature, substrate roughness, etc..
Depending also on energy source, used to heat the coating material to molten o semimolten conditions, thermal spray processes are categorized to; flame spray, electric arc spray, and plasma arc spray.

The coatings are limited by several conditions depending of the *feedstock*, the energy source, the thickness range and the cooling rate. Thermal spray processes are characterized by gradients of both temperature and velocity.

Similar to other deposition techniques this technique also has advantages and disadvantages.

- As advantages; we can apply wide range of materials, deposition of coating without significant heat input and we can use this technique to repair the parts without changing in properties and dimensions.
- As disadvantages by this technique we can only coat what the torch or gun can see and also it is impossible to coat small and deep cavities.

There are also size limitations. It is impossible to coat small, deep cavities into which a torch or gun will not fit.
Coating quality is usually assessed by measuring its **porosity**, **oxide** content, macro and micro **hardness**, **bond strength** and **surface roughness**. Generally, the coating quality increases with increasing particle velocities.

The powder deposited arrives in different positions according to their own inertia. Therefore, some particles take place on different states like unmelted droplets and create porous in between or as “defects” as “unmelts” in the coating.

The level of the possible defects depends definitely on the certain thermal spray process applied, the material selected and the operations conditions used.

Several variations of thermal spraying are distinguished:

- Cold spraying
- Detonation spraying
- Flame spraying
- High-velocity oxy-fuel coating spraying (HVOF)
- Plasma spraying
- Warm spraying
- Wire arc spraying
- Depending on the particles temperature and its velocity we are able to distinguish the several techniques of thermal spray.

Here is a simple graphic showing different techniques for coatings divided by particle velocity (m/s) and temperature (ºC).

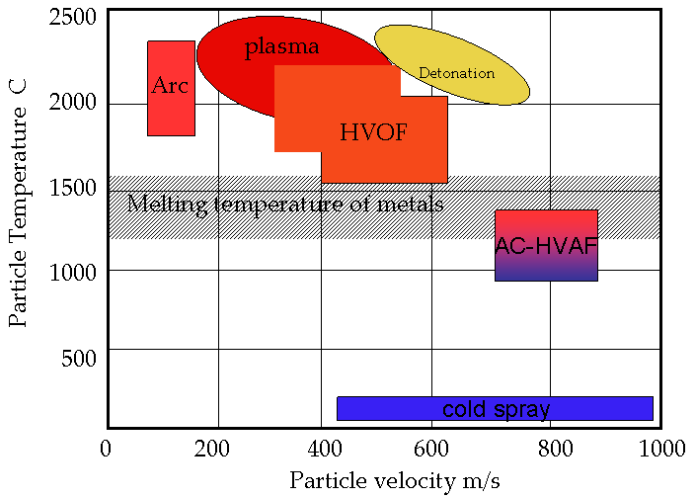


Figure 1.6: ***Particle temperature and velocity in different thermal spray techniques***

(iii) Microstructural Characteristics

The figure 1.7 shows the main characteristics and a typical deposit microstructure. There are created particle size distributions when the wire or the rod feedstock is sprayed as result of non uniform heating and its drag forces.

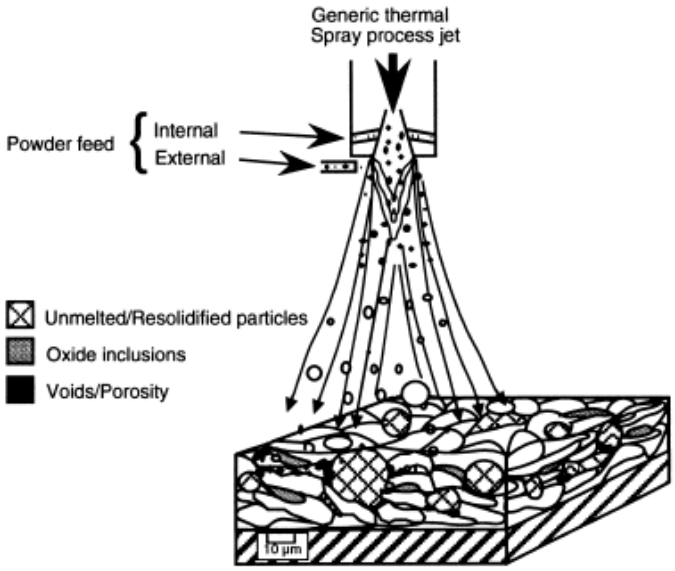


Figure 1.7: Schematic of a typical thermal spray nanopowder process ***(Source: Introduction on Thermal Spray Processing, Handbook of thermal spray Technology)***

The main characteristics of sprayed coatings are related to the oxide distribution, the residual porosity and the grain size. These factors will determine the tensile strength of coatings.

a) OXIDES

Coatings show a distribution of oriented oxides.

The increases in particle velocity of all these processes (wire, arc, plasma and HVOF) lead to different levels of oxide and degrees of oxide dispersion on impact at the surface.

Oxides can raise coating hardness, improve wear resistance and provide lubrication, but an excessive and continuous oxide layers can lead to cohesive failure and contribute to excessive wear rubble. They may even reduce corrosion resistance as well.

When selecting materials and thermal spray process with its conditions it has to be taken into account the possible oxide content and the structure to control the level of oxidation on the subtract.

b) POROSITY

When spraying, the process normally leaves some porosity (between 0-10%) some unmelted (or partially melted) particles, fully melted particles and deformed “splats”. They are meant to be metaestable phases and possible oxidation due to the access of air during the process.

Levels of porosity depend on the spray process, the particle speed, size distribution and spray distance.

Porosity is an advantage when applied in tribological applications since it retains lubricating oil films and it is also good in coatings in biomedical implants. Wear and friction can be also lowered by lamellar oxide layers due to the lubricity of some oxides.

The porosity of thermal spray coatings is typically <5% by volume. The retention of some unmelted and/or resolidified droplets cause to poorer also cohesive strengths, above all in "as-sprayed" cases when no postdeposition eat treatment.

c) GRAIN SIZES

Normally fine grains structures and columnar orientation is achieved.

d) TENSILE STRENGTHS

The tensile strengths of as-sprayed amounts deposited can vary from 10 to 60% (depending of the thermal spray technique). Those techniques which lead to higher oxide levels and lower deposit densities then reach the lowest strengths.

When controlling the atmosphere it can be reached until 60% strength, but it would require post-deposition heat treatment to accomplish the 100%. Low levels of sprayed strengths are consequence of restricted "inter-splat" diffusion and limited grain recrystallization during the quick solidification. The fast solidification also leads residual stress and that limits adhesion and cohesion joints. Accumulated residual stress also limits thickness accumulation.

(iv) Thermal Spray Processes and Techniques

The thermal spray processes are normally divided in these three main categories: flame spray, electric arc spray, and plasma arc spray.

The characteristics of the more commercially major thermal spray processes are given below. Selection of the appropriate thermal spray method is typically determined by:

- Desired coating material
- Coating performance requirements
- Economics
- Particle size and portability.

(v) Materials for Thermal Spray

There are three main materials which are normally used in thermal spray processes:

1. *Single-phase materials*: alloys, intermetallics, ceramics, and polymers

2. *Composite materials*: cermets (WC/Co, Cr3C2/NiCr, NiCrAlY/Al2O3, etc.), reinforced metals, and reinforced polymers
3. *Layered or graded materials*: functionally gradient materials (FGMs)

i. Single-Phase Materials

Metals. Many pure metals and metal alloys are allowed to be thermal sprayed: Tungsten, molybdenum, rhenium, niobium, superalloys, zinc, aluminum, bronze, mild and stainless steels, NiCr alloys, cobalt-base Stellites, cobalt/nickel-base Tribaloys, and NiCrBSi "self-fluxing" alloys.

The advantages of spraying alloys is the possibility of repairing the base metal with a similar spraying material including making them improve their strength, corrosion, wear, and/or oxidation resistance.

Ceramics: Most forms of ceramics can be thermal sprayed, they are:

- *Metallic oxides*: Al_2O_3, stabilized ZrO_2, TiO_2, Cr_2O_3, and MgO.
- *Carbides*: Cr_3C_2, TiC, Mo_2C, and SiC (generally in a more ductile supporting metal matrix such as cobalt or NiCr).
- *Nitrides*: TiN and Si_3N_4.
- *Spinels or perovskites*: Mullite and 1-2-3-type superconducting oxides.

The aim of spraying certain materials is so to provide better properties such wear resistance (Al_2O_3, Cr_2O_3, TiO_2, Cr_3C_2, TiC, Mo_2C, and TiN), thermal protection ($Al2O_3$, ZrO_2, and MgO), electrical insulation (Al_2O_3, TiO_2, and MgO), and corrosion resistance. The most sprayed material is normally ceramics and the plasma sprayed process is its suitable process due to its high temperatures

Intermetallics: TiAl, Ti_3Al, Ni_3Al, NiAl, and $MoSi_2$. The majority of intermetallics are very reactive at high temperatures nut also very sensitive to oxidation, so inert atmospheres should be used during plasma spraying.

Polymers: They also can be thermal sprayed with success always when available in certain forms. A growing number of thermoplastic and thermosetting polymers and copolymers have now been sprayed, including urethanes, ethylene vinyl alcohols (EVAs), nylon 11, polytetrafluoroethylene (PTFE), ethylene tetrafluoroethylene (ETFE), polyetheretherketone (PEEK), polymethylmethacrylate (PMMA), polyimide, polycarbonate, and copolymers such as polyimide/polyamide, Surlyn (DuPont), and polyvinylidene fluoride (PVDF).

The most common processes applied with polymers are flame spray and HVOF.

ii. Composite Materials

Composite and Cermet Materials: Reinforced composites can be produced in various applications. Particulate-reinforced wear-resistant cermet coatings like TiC/NiCr, WC/Co and Cr_3C_2/ NiCr are the most common applications. Thermal spray composite materials may also have *reinforcing phase* where the metal matrix takes place as a binder, supporting the brittle reinforcing phase between from 10 to 90% by volume.

iii. Functionally Gradient Materials (FGM)

FGM is being developed for the production of materials including:

- Uses in applications subject to large thermal gradients,
- Lower-cost coating materials for combinations of corrosion and strength or wear resistance,
- Improvement of electronic material structures for batteries, fuel cells, and thermoelectric energy conversion devices.

The main application for FGMs is *thermal barrier coatings* (TBCs), it minimizes large thermal stresses. Component lifetimes are improved by customizing the coefficients of thermal expansion, thermal conductivity, and oxidation resistance.[3]

1.3.1 HVOF

(i) Characteristics

The mechanism of the HVOF starts with fuel coming into a fuel inlet, which is burnt with oxygen, coming also form another inlet, at a high pressure and generates a high velocity exhausted stream. The powder is injected axially into the jet as suspension in the carrier gas (powder injection port). The gases are burnt in the combustion chamber and flow through the nozzle out of the torch. The combustion chamber and the nozzle are water-cooled (with cooling water).

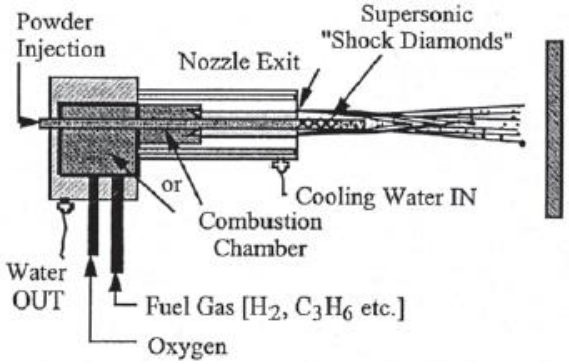


Figure 1.8: HVOF combustion spray. (Graphic from The Int. Thermal Spray As., courtesy of Deloro Stellite INC.)

(ii) Process Parameters: Flame, powder, powder injection, spray characteristics.

FLAME

Working gases: acetylene, kerosene, propane, propylene, hydrogen, methylacetylene-propadiene (MAPP) mixture with oxygen.

The ratio of the gas flow rates determines the temperature of the flame.

The fuel gas flow rates in the range 40-60 Nl/min and the oxygen flow rate correspondingly greater.

Flame temperature: ≈ 2760°C (≈ 5000°F)

POWDER

Powder particle size is usually in the range 5-45μm. The most sprayed particles are carbides.

Other parameters are as in the APS technique

POWDER INJECTION

Powder feed rate is in the range 20-80 g/min.

Powder is injected mostly axially and in some torches radially and nitrogen is used as a carrier gas.

SPRAY CHARACTERISTICS

Spraying distance is in the range 150-300 mm

Fuel gases: Propylene or Propane or Hydrogen

Particle Speed: Up to 4500 ft/s (1400m/s)

(iii) Coating properties

The bond strength of HVOF sprayed carbides can be as high as 90 MPa, the value exceeds the maximum strength of most of the resins. The porosity of HVOF sprayed coatings is lower than 1%. Typical thickness is in the range 100-300μm.[4]

GAS AND LIQUID FUEL HVOF GUN

The HVOF process efficiently combusts oxygen and a gaseous or liquid fuel to produce high kinetic energy with controlled heat input. The coating material, in powder form, is introduced into and uniformly heated by the hot gas stream to a molten or semi-molten condition. The flame and powder are accelerated by a converging / diverging nozzle (air cap) to produce supersonic gas and particle velocities, which propel the powder particles toward the substrate to be coated.

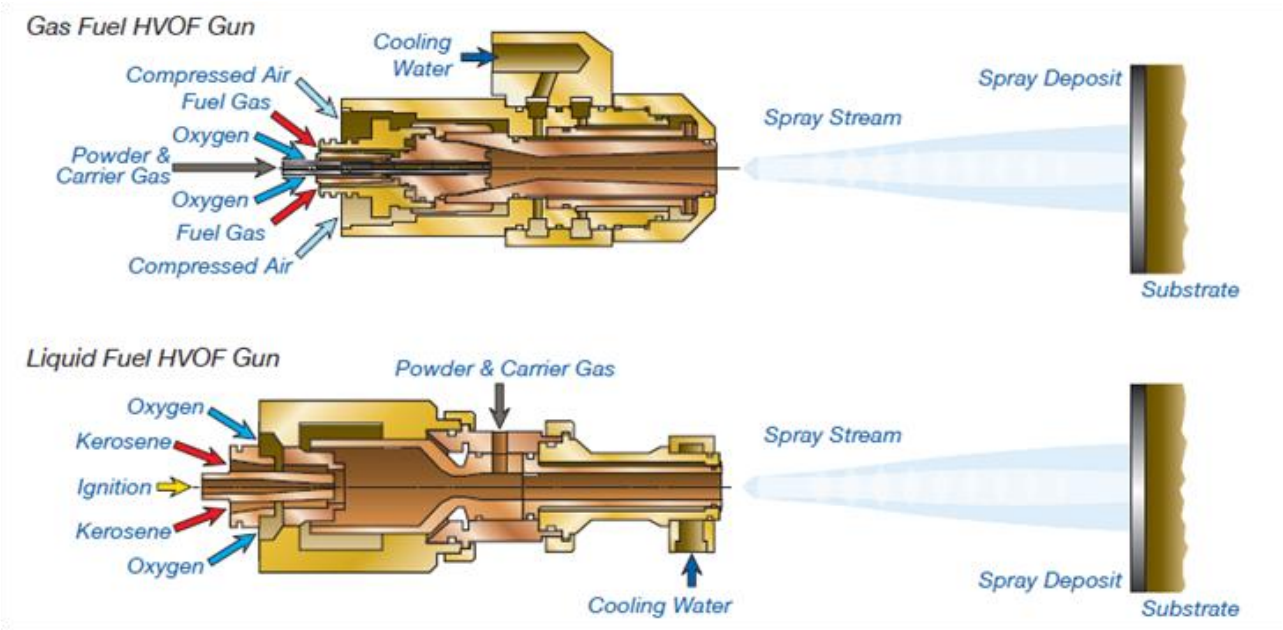


Figure 1.9: Both gas and liquid fuel HVOF gun drawings.

Here are some of the features when spraying with a High Velocity Oxy-Fuel: density, strength, hardness...etc, and its subsequent properties according to this particular technique.

- *High density*. Typical coatings have less than 2% porosity and some others as low as 0.5% porosity.
- *High bond strength*. Several materials sprayed with HVOF have significantly higher bond strengths than the same materials applied using other atmospheric thermal spray processes such as air plasma spray.
- *Optimum Hardness*.
- *Improved Toughness*. Depending on chemistry and other factors, the short dwell time and lower temperatures of HVOF can produce wear resistant coatings with excellent impact resistance.
- *Higher Coating Thickness*. Coatings exhibit greater coating thickness limits than plasma, combustion or wire coatings of the same coating material. These high thickness limits are attributed to a stress relieving 'shot-peening' effect produced by the high velocity particles impacting upon the previous layers of coating.
- *Beneficial Residual Stress*. Compressive residual stresses and, in some cases, very low tensile stresses enhance the fatigue life of a coated component, reduce the susceptibility of cracking and permit greater coating thickness limits.

- *Excellent Wear Resistance*. HVOF coatings can exhibit superior resistance to sliding / adhesive wear, fretting, erosion or cavitation depending on the material and process parameters chosen.
- *Superb Corrosion Resistance*. The high density and exceptional metallurgical properties of HVOF coatings provide enhanced resistance to the effects of corrosion, including hot corrosion, oxidation and the effects of corrosive media such as acidic and alkaline atmospheres and liquids.
- *Fine Surface Finishes*. Smooth surfaces finishes allow HVOF-produced coatings to be used in the as-sprayed condition for many applications. Coatings can be machined, ground, lapped, honed or super finished to produce very high surface finishes to precise tolerances.[5]

1.4.Coatings protecting from Corrosion and Wear

Surface coatings can improve product performance, increase productivity and improve lifecycle costs.

1.4.1 Coatings for Corrosion

Environmental factors and reactions to industrial chemicals can severely degrade the life expectancy of metal components. There are numerous corrosion resistant coating options to help combat the effects of corrosion and reduce the associated costs and time delays. The optimum solution will depend on the circumstances and the nature of the problem.

(i) The Corrosion Process

Corrosion is an electrochemical process in which a metal reacts with its environment to form an oxide or other compound. The cell which origins this corrosion process has three essential components:

1. Anode; is the location at which the metal is corroded.
2. Cathode; is the corrosive medium.
3. Electrolyte (electrically conducting solution); it is part of the same metal surface, or of another metal surface in contact with it, it forms the other electrode in the cell and is not consumed in the corrosion process.

At the anode the corroding metal passes into the electrolyte as positively charged ions, releasing electrons which participate in the cathodic reaction. Hereafter the corrosion current anode-cathode consists of electrons flowing in the metal and ions flowing in the electrolyte.

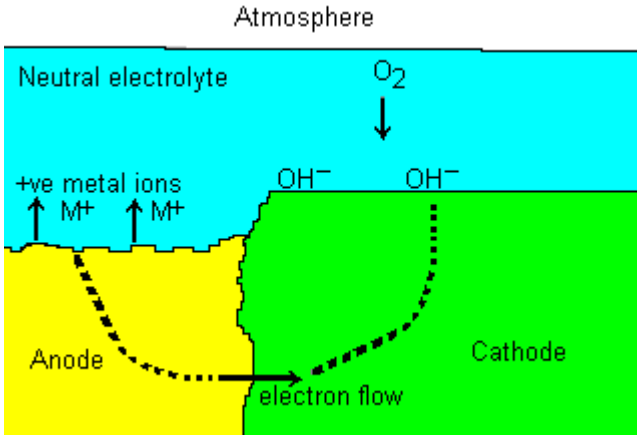


Figure 1.10: Corrosion mechanism between 2 surfaces

The surface of one component may become the anode and the cathode will be the surface of another component in contact with it. Frequently, corrosion cells will be much smaller and more numerous, occurring at different points on the surface of the same element. Anodes and cathodes may arise from differences in the constituent phases of the metal itself, from variations in surface deposits or coatings on the metal, or from variations in the electrolyte.

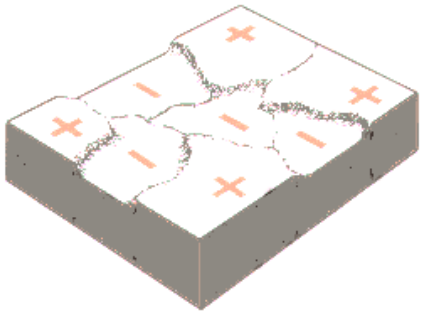


Figure 1.11: Same surface with different anodes and cathodes on it

The metal may be immersed in an electrolyte or the electrolyte may be present only as a thin condensed or adsorbed film on the metal surface. The proportion of corrosion is influenced substantially by the electrical conductivity of the electrolyte.

An imperfect coating might lead to corrosion as well. The current generated passes from one material to the other by the path of the lowest resistance and returns to the first one through the solution by the passage of ions. The material with the greatest negative potential dissolves and it's called the anode, and the other one will be the cathode.

The size of the cathode relative to the anode is important, on the other hand, a large cathode coupled to a small anode has the opposite effect, with quick attack of the anode.

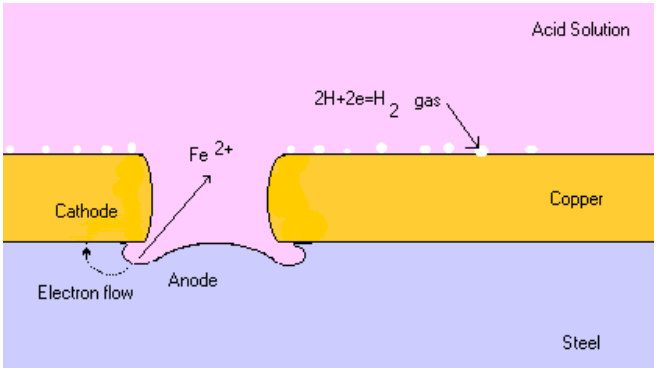


Figure 1.12: Corrosion of steel as a consequence of a bad coating of its copper layer

- **Pitting and crevice corrosion**

Electrochemical corrosion can be motivated also from dissimilarities in the electrolyte.

Cavities in metal surfaces and metal surfaces partly covered by another material are led to this sort of attack. The diffusion of oxygen into cavities or crevices is hindered and oxygen can reach easily the surrounding metal leading these areas becoming anodic. The metal ions made in the cavity migrate outward and react with the hydroxide ions flowing in the opposite way to form a corrosion product (*rust)* at the beginning of the cavity.

This position of the corrosion product provokes more corrosion by making the diffusion of oxygen to the anode more difficult, and if the cathodic area is big severe pitting may arise. Also when dry conditions prevail moisture can be stuck in the cavities letting corrosion to continue.

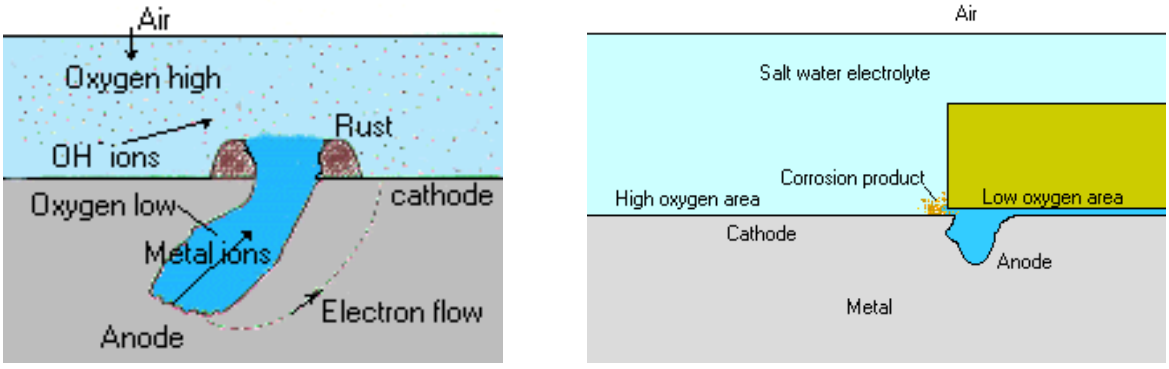


Figure 1.12: Corrosion provoked by differences on the electrolyte

Normally very corrosion resistant materials can suffer from this type of corrosion attack relying on thin oxide films for protection. These materials count on oxygen being present, so that

they can keep their oxide films. When oxygen is excluded and the oxide films break down, the material surface becomes active and corrodes.

The effects of corrosion can be accelerated or persuaded when working with stress and various wear mechanisms. Regularly the mechanisms work by not allowing the corroded metal to become passive by continually removing protective films and setting up active/passive corrosion cells where the mechanism is not even applied. The corrosion products formed may provide abrasive remains to make matters worse.

- Corrosion fatigue
- Cavitation corrosion
- Erosion corrosion
- Fretting corrosion
- Stress corrosion cracking [6]

(iv) Coatings for Corrosion Protection

Metallic coatings of mostly any metal can be spread on metallic substrates for the purpose of decoration, modification of physical properties of the substrate, corrosion reduction of the substrate, or any combination. Metallic coatings for the express purpose of corrosion protection will be examined, although the corrosion characteristics of any thin metallic coat must be considered, regardless of its intended use, since corrosion may ultimately alter its intended property.

Principles of Corrosion Protection by Metallic Coatings

If the metallic coating has no discontinuities, then the corrosion properties of only the coating itself would be the principal matter. However, metallic coatings are frequently porous as a result of the manufacture method and, even when contiguous, have physical defects because of mechanical or corrosion damage during service that eventually expose the underlying substrate metal. Therefore, the anode/cathode relationship between the coating and substrate becomes of principal concern. An intermediate coating could also be necessary for coating formation.

Commercial metallic coatings can be either anodic or cathodic to the substrate. The basic principles of galvanic corrosion say that the common relationship is having a small cathodic area and a large anodic area. Anodic coatings protects exposed areas, until the coating surrounding the access

spot recedes and the area of the exposed substrate exceeds the capacity of the coating to keep the cathodic polarization. At this point, the substrate will begin to corrode.

In the case of a cathodic coating, the presence of coating defects is compensated by introducing numerous defects to increase the anodic area, e.g., chromium coatings.

- **Specific Systems Used to Form Coatings**

Zinc Coatings

Zinc is an easily applied, cheap, and efficient coating on steel against corrosion. It represents one of the most frequently used metallic coatings. It is used widely in buildings, cars, marine structures, and the infrastructure. Zinc can be applied by hot dip galvanizing, spray application, electroplating, and sherardizing. Zinc-acting layers can also be applied via use of a zinc-rich organic paint. The life of the coating will be established by the thickness of the Zn layer. The thickest ones will be created by the hot dipping and spraying method. The thickness of the zinc coating will be a function of the surface pretreatment of the steel, the dipping procedure and the type of steel. Also the temperature and time of can also affect alloying. Hot dipping and sherardizing will perform the most important alloying, which can influence the hardness, density, and corrosion properties of the resulting coating. In some cases, elements can be added to the zinc (e.g., aluminum) to minimize alloying and improve the corrosion protection in certain environments. Zinc is a reasonable corrosion resistant in most atmospheres thanks to the materialization of protective corrosion products, and it is also anodic to steel. So, in addition of becoming an anode when breached, the corrosion products of zinc can plug the breach and slow the corrosion process. Protective oxides are stimulated as well in certain sea waters with magnesium salts and it is used widely to protect buried structures, although it doesn't behave that well in alkaline soils and some cementitious environments. Zinc may be further protected by following treatments such as chromate conversion coating or painting.

- Zinc has been always alloyed with aluminum to produce coatings with improved corrosion resistance, bigger formability, and better paint adhesion.

Tin and Tin Alloys

Tin coatings can be spread over a wide range of alloys (e.g., steel, copper, and brass) because of their resistance to corrosion in every pH condition, low toxicity, ease of welding, and lack of catalytic activity of corrosion products.

They can be produced by hot *dipping, electrodeposition,* and *spraying*.

- *Hot dipping* performs coatings under 25μm thickness and with a notable alloy layer or intermetallic created between the tin and substrate. Hot-dipped coatings will typically have penetrating porosity.
- *Electrodeposited coatings* can be applied to a larger thickness therefore penetrating porosity is not a restrictive factor. Those coatings will not have an alloy layer unless the coating is reinforced by momentary surface melting. Sprayed coatings must be applied to a big thickness (350μm) to remove the threat of penetrating porosity; however, the porosity in a thinner coating may be closed by use of mechanical abrasion.

Reactions between some tin coatings and some substrates can occur, but usually do not compromise corrosion protection. In those cases, an undercoating of another metal or alloying of the tin may be used to limit the reaction.

Tin coatings are used extensively in food and beverage containers, copper wire, large vessels in the food industry, toys, and kitchen equipment. Tin may be alloyed with a number of metals for purposes of improving weatherability in atmospheres containing sulfur (lead), elimination of the alloy layer (zinc), and improved hardness (nickel).

Aluminum Coatings

Aluminum and some of its alloys are used to protect steel and high and medium strength aluminum alloys from corrosion. These coatings are used in marine requests, steel pipes, gas cylinders, transmission lines, and several infrastructure and transportation applications. This material can be applied by *arc-spraying*, *hot-dipping*, or *cladding*, along with numerous other vacuum, gaseous, chemical vapor, and diffusion methods and combinations of these (e.g., spray aluminizing). Aluminum can also be electrodeposited from organic solvents (e.g., aluminum trichloride and lithium aluminum hydride in diethyl ether) and molten salts (e.g., fused aluminum chloride melts).

Aluminum coatings on steel are chosen over zinc in hostile environments such as marine, industrial, or acidic environments and they also last longer. Porous aluminum coats produced by spray application protect thanks to the anodic action. But in the initial stages some corrosion of the steel may occur and produce superficial red rust on the aluminum coat surface. Aluminum corrosion products consequently seal the coating pores.

It has been suggested that the initial rust staining can be reduced or removed by using aluminum-zinc alloys, however, numerous tests in the aggressive environments mentioned above indicate that aluminum, and not its alloys, remains the best choice. Aluminum coatings on steel symbolize an exceptional substrate for paint and can prolong the repaint interval significantly. The corrosion protection of aluminum can be enhanced in certain environments by the addition of zinc.

The adding of silicon increases the solubility limit of iron in aluminum and therefore reduces the thickness of the intermetallic layer that forms.

Cadmium Coatings

Corrosion protection by cadmium is by barrier exclusion when contiguous coatings are employed, and by sacrificial action when there are gaps in the coating, characteristic or physical breaches.

Cadmium is the perfect coating for marine atmospheres and offers better protection than zinc. Less cadmium is needed thanks to its higher efficient galvanic protection, best application when fine tolerances are necessary. However, the toxicity of cadmium has limited its use to special applications, and has encouraged the progress of replacement coatings. Despite toxicity issues, cadmium has several advantages over zinc. Cadmium carbonate and cadmium chloride have lower solubilities than the similar corrosion products of zinc, therefore giving more protection to cadmium in marine environments. Cadmium is also easier to weld and has a lesser electrical contact resistance.

Cadmium coatings are used on steels, stainless steel, copper-based alloys, and titanium to prevent galvanic corrosion of these base metals and aluminum and magnesium alloys.

Copper-based Coatings

Copper coatings by themselves are not frequently used for corrosion protection, but can be used as a thin interlayer to improve the corrosion resistance of other coatings (e.g., nickel) by increasing the covering power. It is not an effective interlayer for all metal coatings.

Copper and copper alloys are applied as decorative finishes, as a help in electrical conduction, as a protective layer against fretting corrosion, and as an undercoat for other metal coatings on steel and zinc-based castings. As an undercoat application, copper is less critical than steel in terms of cleaning and provides better adherence to nickel deposits. Copper is normally applied via *electrodeposition*, sometimes applied by *flame spraying* and *electroless plating* too. The corrosion protection properties of copperbased coatings are very dependent on the homogeneity of the deposit, like cathodic coatings. The porosity is minimum when the surface and plating bath are kept clean and with no impurities, both solid and dissolved.

For example, copper is not recommended for chromium coatings. Other alloys of copper that are used in interlayer applications include: copper-zinc, copper-tin, copper-nickel, copper-cadmium, copper-gold, copper-lead, and copper-tin-zinc.

Nickel Coatings

Most nickel is consumed in decorative purposes as an interlayer for chromium coatings, only a small percentage is used in engineering applications. However, nickel coatings are generally applied to steel, zinc, and other metals to provide protection against corrosion, erosion, and abrasion.

Nickel coatings are commonly electrodeposited from Watts-type solutions consisted of nickel sulfate, nickel chloride, and boric acid. Nickel is also electrolessly deposited. The corrosion resistance of the electrodeposits is characteristically better than the electroless deposits, but the electroless deposits have the advantage to make it easier depositing on complex shapes and internal surfaces. Nickel coatings are corrosion resistant to a range of chemical environments., although nickel is not recommended for exposure to chlorine, sulfur dioxide, nitric acid, sodium hypochlorite, and salts of silver and mercury. Nickel coatings for corrosion protection may need to be 120-130μm in thickness, unless machining is required. Although applied for esthetic reasons, some advantage is gained in corrosion protection by the double-layer nickel coating used in decorative applications. These coatings have a sulfur-free nickel undercoat that is cathodic to the bright nickel topcoat. Corrosive attack is then favorably directed to the surface, and penetration to the substrate metal is delayed significantly.

The use of nickel coatings must consider the effects on other material properties. Nickel coatings are known to have an influence on fatigue strength, corrosion fatigue, galling, and fretting corrosion.

Chromium Coatings

Chromium has a high resistance to corrosion, it becomes an attractive material to apply as a thin coating to less resistant metals, despite the difficulty of processing and machining bulk chromium. Chromium is protected by a thin but stable and tenacious oxide, Cr_2O_3, *chromia*, able to resist high-temperature oxidation and been exposed to most atmospheres, including H_2S and SO_2.

It is a extremely reflective coating having an esthetic appeal, and is also really hard, making it the perfect candidate for coatings calling for resistance to abrasion and wear.

Chromium coatings are generally applied via:

- *Electrodeposition* (most widely used for metallic coating production)
- *Chromizing*
- *Vapor deposition methods* (used only in special high-temperature applications where a completely nonporous coating is needed)

Chromium is typically plated from a chromic acid bath containing a small amount of sulfuric acid. Although, it has to be taken into account trivalent chromium solutions due to hazards associated with hexavalent chromium.

Electrodeposited chromium can be either α-b.c.c. or β-h.c.p. The form is converted to the form upon heating or storage at room temperature. The electrodeposit is either *porous* when the plate is thin (0.5μm), or *cracked* when thicker.

Other types of chromium electrodeposits include *hard* and *black chromium deposits*.

- *Hard chromium platings* are simply thick deposits applied to carbon and alloy steels, cast iron, and light alloys to provide wear, abrasion, and corrosion resistance. They are typically lapped or machined before use, so allowances must be made.
- *Black chromium plating* is often used in the optical and instrument industries. It is typically not just chromium and contains a large amount of chromium oxide. Some of the black chromium deposits have excellent corrosion protection.

When the substrate is polished the corrosion resistance of chromium electrodeposited gets better, but a nickel interlayer is sometimes applied because of the expense of polishing. However, when a wear- and abrasion-resistant coating is needed, a hard coating is applied directly onto the steel. The chromium electrodeposit will be cracked to expose the underlying substrate material unless it is very thick.

Corrosion is placed in anodic substrate, whether it is steel or nickel. This localized form of corrosion can be avoided by creating crack-free deposit by:

1. Putting on a thicker deposit under normal hard plating conditions, or,
2. Using a higher current density process with a bright plating solution at slightly elevated temperatures.

The corrosion properties of chromium-plated materials have also been improved via the use of micro-cracked coatings which have high crack ratio (30-80cracks mm^{-1}), to increase the anodic area and thus reduce the anodic current density. A more interesting method for improving the corrosion resistance is to apply a porous chromium layer by the use of inert particles in a nickel underlayer.

However, Cr_20_3 scales are frequently formed on the surface of the chromium-bearing alloys at high temperatures to protect the alloys. The addition of active elements such as Yttrium to the alloys is recognized to increase the adherence of protective Cr_20_3 and improve the oxidation resistance of the alloys. That could be the main reason why we are using Cr_2O_3 with YSZ8 as a corrosion protector.

Many attempts have been made in order to understand the growth mechanism of Cr_20_3 scales and the effect of yttrium, like determining diffusion coefficients of oxygen and chromium in Cr_20_3. It has been shown that oxygen diffusion was slower than chromium diffusion by about 3 orders of magnitude. Later, from oxidation studies, it was concluded that the Cr_20_3 scales on the chromium metal grow by *counter-current diffusion* of chromium and oxygen, mainly via the grain boundary. It was then suggested that outward cationic diffusion is more important for the growth of undoped Cr_20_3 scales.[7]

1.4.1. Coatings for Wear

Protective Coatings for Abrasion and Wear Resistance: There are a number of wear mechanisms which can reduce the working life of metallic parts. Actions such as fretting, sliding, vibration, friction, galling and erosion will result in wear on a component.

The solution to the component wear problems will depend on the specific circumstances, but there are several alternatives. It may involve the application of a harder substance which will endure the mechanical actions placed on the part.

(i) Wear

Wear is very complex mechanism. The real area of contact between two solid surfaces compared with the apparent area of contact is always very small, being limited by the points that make contact between surface asperities. The load applied to the surfaces will be reassigned through these points of contact and the localized forces can be quite large. Surface properties such as hardness, strength, ductility, work hardening etc. are very important factors for wear resistance, but other factors like surface finish, lubrication, load, speed, corrosion, temperature and properties of the opposing surface etc. are equally important.

- Abrasive Wear

The *abrasive wear* mechanism is essentially the same as machining, grinding, polishing or lapping that we use for modeling materials. Two body abrasive wear occurs when one surface (usually harder than the second) cuts material away from the second. Abrasives can act as in *grinding* where the abrasive is attached to one surface or as in *lapping* where the abrasive drops producing a series of indentations as opposed to a scratch.

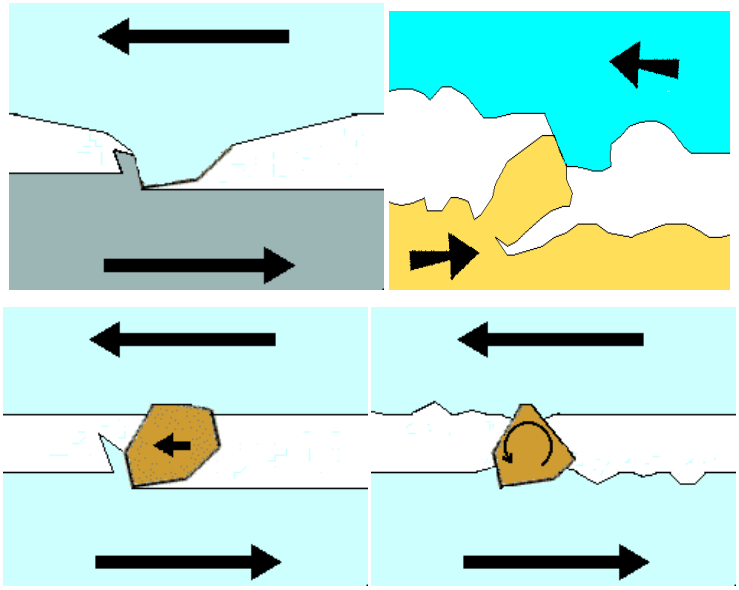


Figure 1.13: Different mechanisms that lead to surface wear

- Adhesive Wear

Adhesive wear is created by the formation and shearing of welded junctions between two sliding surfaces. It is necessary for the surfaces to be in close contact with each other to occur the adhesive wear.

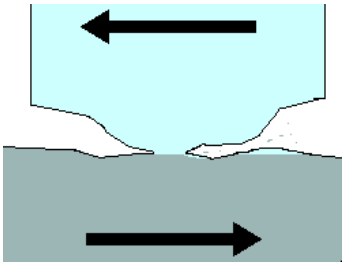


Figure 1.14: Shearing points of contact or asperities provoking adhesive wear

- Erosion

Erosion is caused by a gas or a liquid which may or may not carry entrained solid particles which affect the surface. When the angle of impingement is small, the wear produced is comparable to abrasion. When is normal to the surface, material is displaced by plastic flow or moved by brittle failure.

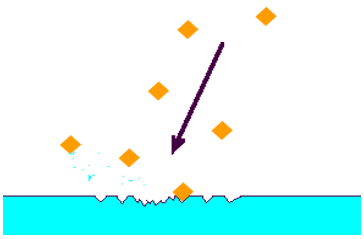


Figure 1.14: Impurities coming from the surroundings causing erosion

- Cavitation.

Cavitation, inside a liquid, is the formation and collapse of cavities or bubbles that contain vapour or gas. It is normally originated from changes in pressure in the liquid produced by turbulent flow or by vibration, also from changes in temperature (boiling). It occurs when bubbles or cavities collapse on or very near the eroded surface

- Fretting Wear

Fretting is cause by oscillatory movements, usually tangential, between two solid surfaces in contact. It occurs when frequent loading and unloading causes cyclic stresses which make surface or subsurface break-up and loss of material. Vibration is a common cause.

(ii) Reducing Wear by Using Thermal Spray Coatings

Thermal spray coating has been always used to maintain and repair a wide range of surfaces to avoid wear. The advantages can be chosen from the bulk requirements to be it strength, weight or cost without the need to consider its wear resistance or other surface properties.

Selection of the best coating for an application is sometimes complicated. For instance, HVOF tungsten carbide/cobalt, plasma sprayed chromium oxide ceramic or fused coatings as giving the ultimate performance can be used.

Coatings provide the best solution to many applications, but they are certainly not universally matching with all applications, some other factors must be considered:

- Cost
- Life expectancy
- Corrosion
- Counter surface
- Effect of process on substrate material
- Surface finish or profile
- Temperature
- Lubrication
- Abrasives
- Loads and speeds
- Impact, shock or fatigue
- Ability to work harden

- Severity and angle of attack
- Coefficient of friction
- Porosity
- Other specific coating properties may be required
    - Thermal barrier or conductor
    - Electrical insulator or conductor
    - Non-magnetic
    - Special surface profiles
    - Abradable (requiring erosion resistance, but sacrificial to counter surface)
    - Abrasive (required to abrade or grip counter surface)
    - Very low coefficient of friction or non-stick properties

- **Thermal Spray Coatings for Soft Bearing Surfaces**

Coatings of a *soft bearing material* allow abrasive particle inlays and permit deformation to reorganize some misalignment of the bearing surfaces. These surfaces require being lubricated and should be low in cost as they wear in before the other surface (usually very much harder). Some of these coatings are quite porous with the advantage that they act as reservoirs for lubricants. The following coatings are commonly used:

- Aluminium bronze
- Phosphor bronze
- White metal or babbitt
- Aluminium bronze/polymer composites

- **Thermal Spray Coatings for Hard Bearing Surfaces**

When the embedding of abrasive particles and self-alignment are not necessary, and no a lot of lubrication required we are peaking about hard bearing materials. Thermal spray coatings provide added benefits over wrought/cast materials thanks to the porosity acting as a lubricant reservoir and the composite nature of included oxides and amorphous phases. Some coatings don't have much macrohardness, but very often show improved wear resistance. The following coatings are commonly used:

- Cermet coatings like tungsten carbide/cobalt and chromium carbide/nickel chromium
- ***Oxide ceramics like chromium oxide and alumina***
- Molybdenum

- Various hard alloys of iron, nickel, chromium or cobalt

- **Thermal Spray Coatings for Resistance to Abrasion**

Ideally, the material should have a hardness that is in excess of that of the mating surface or abrasive particles. The following coatings are commonly used:

- Cermet coatings like tungsten carbide/cobalt
- Chromium carbide/nickel chromium (particularly for high temperatures above 540 C)
- ***Oxide ceramics like chromium oxide and alumina***
- Fused self fluxing alloys (NiCrSiB)
- Various hard alloys of iron, nickel, chromium or cobalt

- **Thermal Spray Coatings for Resistance to Fretting and Surface Fatigue**

Coatings resistant to wear caused by repeated sliding, rolling, impacting or vibration are the ones interesting. Generally coatings with good toughness and low residual tensile stress are best. The following coatings are commonly used:

- Cermets coatings like tungsten carbide/cobalt
- Chromium carbide/nickel chromium (particularly for high temperatures above 540 C)
- Fused self fluxing alloys
- Aluminium bronze
- Copper nickel indium
- Various alloys of iron, nickel, chromium or cobalt

- **Thermal Spray Coatings for Resistance to Erosion**

The selection of coating for erosive wear is dependent on the severity and type of erosion. For solid impingement erosion at a shallow angle of attack where the wear is similar to that of abrasion, high hardness coatings are required. For solid impingement angles near 90 coating toughness becomes more important. For cavitation and liquid impingement generally, a coating with good surface fatigue resistance is needed. The following coatings are commonly used:

- Cermets coatings like tungsten carbide/cobalt
- Chromium carbide/nickel chromium (particularly for high temperatures above 540 C)
- Fused self fluxing alloys
- Non ferrous alloys, aluminum bronze, monel
- ***Oxide ceramics like chromium oxide and alumina***

- Various alloys of iron, nickel, chromium or cobalt

- **Coatings for Low Friction and Non-stick Properties**

PTFE polymer type materials have extremely low coefficient of friction and are "non-stick" to most materials. These particular properties are very useful, but these materials have very low strength and very poor wear resistance. Combination coatings are the ones where thermal spray coatings are used to provide the mechanical support and keying for the polymer and to provide the wear resistance, make for an extremely effective compromise.

1.4.2. Properties and Characteristics

Pure chromia, as a mineral, Chromium (III) oxide (Cr2O3), is a raw inorganic compound material. It's a fine pigment obtained in a chemical way form chromic iron ore. It exits as one of the principal oxides of chromium.

In nature, it can be found within the mineral *eskolaite*. Cr_2O_3 structure is corundum, a crystalline way of compactation based on hexagonal close packs of layers of oxide anions with its 2/3 of its spaces occupied by chromium. It is defined as a hard, brittle material, antiferromagnetic up to 307K and not easily attacked by acids or bases.[8]

- **Properties of Chromia**:

CAS number*	[1308-38-9]
Molar mass	151.99 g/mol (Cr=68.43%, O=31.57%)
Density	5.22 g/cm3
Melting point	2435, 2708K 4415K
Boiling point	4000, 4273, 7232K
Solubility in other solvents	Negligible (Insoluble)
Hardness	2955 kg/mm/mm (VH)
Thermal conductivity	9.99-32.94 W/m/K
Heat of fusion	27,6 cal/g (4200 cal/g mol)
Transition temperature	2538°C

*CAS number: Chemical Abstract Service registry number

Table 1: Chromia properties [9]

Chromium oxide coatings are chemically inert, have high mechanical strength, hardness and good optical characteristics. This is why they have been extensively used in many applications

including corrosion protection, wear resistance, electronics, and optics. Cr_2O_3 is well suited for *wear resistance* applications and *coating for corrosion protection*, as it is one of the hardest oxides with 29.5 GPa hardness.

Numerous deposition techniques have been tried for making these coatings. Cr_2O_3 coating hardness can vary substantially due to compositional and microstructural variations, depending on the deposition method.

Coating mechanical, adhesion and wear properties are strongly affected by microstructure. Interfaces with high adhesion ear known to ensure prolonged coating life and good wear resistance. Sputtered coating microstructure and physical characteristics depend on the deposition parameters. Also, substrate surface conditions prior to deposition, characterized y surface roughness, stress and oxidation state, play an important role in controlling coating properties[10]

1.4.3. Sintering Aids

One of the solutions proposed in HIPECO 2 project was the possibility of mixing the Cr_2O_3 agglomerates with another secondary, lower melting ceramic (TiO_2, Y_2O_3..)
Due to poor sintering properties (need high sintering temperature) the Cr_2O_3 cannot resist air classification without degradation for subsequent tests, which leads this to improve particle strength as well. Though in higher sintering temperature there is also risk of grain growth.

Yttria-stabilized zirconia (YSZ) appeared to be a good sintering aid for the Cr_2O_3, an additive that could improve consequent properties of the coating.

- **Yttria-stabilized zirconia (YSZ)**

Yttria-stabilized zirconia (YSZ) is a zirconium oxide (ZrO_2) based ceramic, where the particular crystal structure of zirconium oxide is made stable at room temperature by an addition of Yttrium oxide is ($\mathbf{Y_2O_3}$). These oxides are called "*zirconia*" ($\mathbf{ZrO_2}$) and "*yttria*" ($\mathbf{Y_2O_3}$).

The addition of yttria to pure zirconia replaces some of the Zr^{4+} ions in the zirconia structure with Y^{3+} ions. This produces oxygen vacancies, as three O^{2-} ions replace four O^{2-} ions. It also permits yttrium stabilized zirconia to conduct O^{2-} ions, provided there is enough vacancy site mobility, a property that increases with temperature.

Applications: Yttria-stabilized zirconia is known for its hardness and chemical inertness and as a **refractory** ceramic.

- It can work as a **thermal barrier coating** and as an **electroceramic** due to its ion-conducting properties.
- Used in the production of a solid oxide fuel cell, YSZ is used as the solid electrolyte, which enables oxygen ion conduction while blocking electronic conduction.
- For its hardness and optical properties in monocrystal form it can be used as part of jewel production.
- YSZ doped with rare-earth materials can act as a thermographic phosphor and a luminescent material.[11]

YSZ Coatings

In a conventional yttria stabilized zirconia (YSZ) coating, the porosity may be classified into several groups; intrasplat vertical cracks, intersplat voids and spherical pores.

Nanostructured YSZ plasma spray coatings have shown promise in extending the performance of coatings. In the nanostructured YSZ, a developed agglomerate morphology with a particle size below 1 μm increases the strain accommodation ability.

Therefore, the elastic modulus is lower and irreversible deformation occurs by particle sliding and micro-cracking that is distributed over the volume of the deformation zone. The superior resistance to cracking has been investigated by an indentation method.

The nanostructured YSZ/conventional YSZ coatings being investigated in the current study are designed to improve the performance of multilayer thermal barrier coatings. Those coatings are designed to provide several functionalities such as oxidation and thermal protection.

The coating porosity depends on the level of melting of powder particles during deposition. Usually, a bimodal morphology of the nanostructured YSZ is observed; combining regions of particles that are fully molten or partially molten.

However, a very dense microstructure can also be achieved with deposition parameters that provide full particle melting. A wide range of different microstructures may be produced depending on the deposition technique and spray parameters used. This variability includes not only changing the distribution of a certain type of porosity but also a distinct modification of the microstructural character.

A goal in the application of these nanostructured coatings may be coarsening of the nanoparticles and sintering due to the high surface area if this material is exposed to the most harsh thermal conditions.

The top dense layer is designated to be more resistant to sintering and provides an initial thermal barrier for the following porous layer that retains the beneficial properties of the nanostructured YSZ. The dense top layer can be manufactured either from a conventional YSZ or a nanostructured feedstock since either of the materials can be deposited as a very dense microstructure under suitable deposition conditions.

One way to moderate any sintering effect is infiltration of the material with an anti sintering agent.[12]

2. Material and Experimental Methods:

2.1.Powder Manufacturing

A market research was developed to find the finest particles size between Cr_2O_3 producers.

To be able to spray effectively with HVOF the size distribution needs particles to be among 15-25 µm. Bayer® was elected to be the main dealer for the Cr_2O_3 powders (300nm) and Inframat® the chosen one to provide us the powers of YSZ (30-60nm).

In this research we will test different kind of powders Cr_2O_3 with different percentages of YSZ8 (ZrO_2 –8mol-%Y_2O_3) to be able to measure mechanical properties after mixing and sintering the powders. Sintering and characterization of these diverse Cr_2O_3-based powders will be the main goal in this study.

Granules were processed by agglomeration of Cr_2O_3 with different YSZ additions:

- Cr_2O_3 (no aids added)
- Cr_2O_3+5 vol-% nano YSZ8
- Cr_2O_3+15 vol-% nano YSZ8
- Cr_2O_3+50 vol-% nano YSZ8

Each of them labelled with names related to the project, HIPECO2, HPC01"X". In total, powders plus tags and particles sizes are shown in the next table.

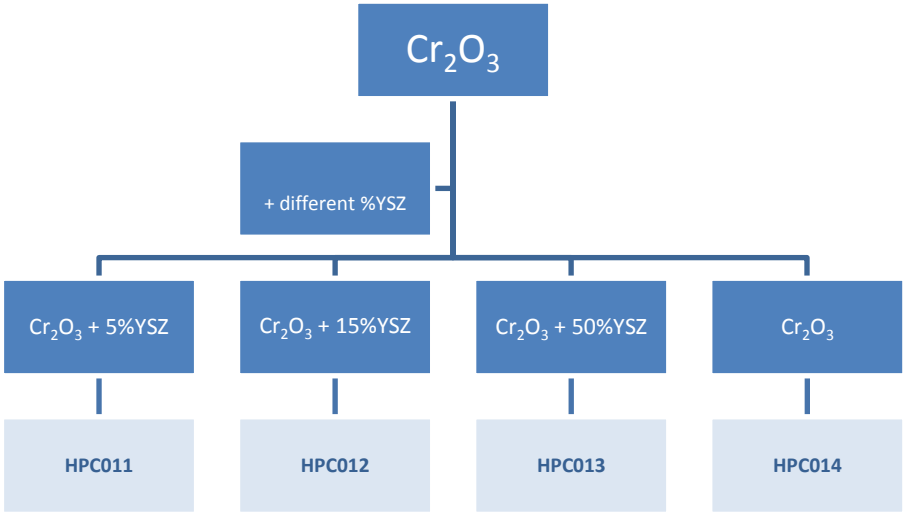


Figure 2.1: Diagram of every powder labelled

A thin layer will be produced with these compositions. So far, just Cr_2O_3 coatings have been studied and its properties analyzed.

Chromium Oxide Coatings

Chromium oxide coatings, without YSZ additions, are chemically inert, have high mechanical strength, hardness and good optical characteristics; therefore, they have been widely used in many applications including corrosion protection, wear resistance, electronics, and optics. Cr_2O_3 is well suited for wear resistance applications, as it is one of the hardest oxides with 29.5 GPa hardness.

Several deposition techniques have been tried for making these coatings. The Cr_2O_3 coating hardness can vary substantially due to compositional and microstructural variations, depending on the deposition method. Hardness of a plasma-sprayed Cr_2O_3 coating, 50 nm thick was about 14.7 GPa, while a 200 nm thick RF-sputtered chromium oxide coating, stoichiometrically close to Cr_2O_3, exhibited 30 GPa hardness combined with good scratch resistance. Even for the bulk Cr_2O_3, hardness values reported were from 9 GPa to 29.5 GPa. Hones et al.[13] investigated a correlation between the hardness and the sputtering deposition parameters, i.e. oxygen partial pressure and substrate temperature, and found favourable deposition conditions with an oxygen partial pressure of about 15–20% of the total sputtering gas pressure at substrate temperatures exceeding 500 K.

Coating mechanical, adhesion and wear properties are strongly affected by microstructure. Interfaces with high adhesion are known to ensure prolonged coating life and good wear resistance. Sputtered coating microstructure and physical characteristics depend on the deposition parameters. Also, substrate surface conditions prior to deposition, characterized by surface roughness, stress and oxidation state, play an important role in controlling coating properties.[14]

2.2.Agglomerations and Sintering

All the powders labelled above, Figure 2.1, with their own compositions will be sintered now. It was decided to use two types of sintering atmospheres to subsequently check all the possible properties out.

Argon with 6% H_2 additions is a quite common atmosphere for sintering nanopowders although it is expensive due H_2's high costs in the market. This atmosphere was selected for sintering at 1100, 1200, 1300ºC. On the other hand it will be spread N_2, at least 6 times cheaper, as another sintering atmosphere, this time tested in 1200ºC.

Slurries were manufactured by bead mill and spray-dryed with Niro Spray Dryer P-6.3.

Table2.1. shown below shows all the possible compositions of granulated Cr_2O_3 that will be sintered with their atmospheres and temperatures.

Powder code	Composition	Raw materials	Particle size (cyclon), µm	Sintering tests	
				Atmosphere	T (°C)
HPC011	Cr_2O_3+5 vol-%YSZ8	Cr_2O_3 Bayer GN-M, 300nm; YSZ Inframat, 30-60 nm	7-28	N_2	1200
				Ar-6% H_2	1100, 1200, 1300
HPC012	Cr_2O_3+15 vol-%YSZ8	Cr_2O_3 Bayer GN-M, 300nm; YSZ Inframat, 30-60 nm	7-27	N_2	1200
				Ar-6% H_2	1100, 1200, 1300
HPC013	Cr_2O_3+50 vol-%YSZ8	Cr_2O_3 Bayer GN-M, 300nm; YSZ Inframat, 30-60 nm	7-26	N_2	1200
				Ar-6% H_2	1100, 1200, 1300
HPC014	Cr_2O_3	Cr_2O_3 Bayer GN-M, 300nm	6-25	N_2	1200
				Ar-6% H_2	1100, 1200, 1300

Table 2.1: Samples codes with their sintering conditions

The binder used was a polymeric one, under patent, that burns off at 400ºC.

2.2.1. Agglomerates and Sintering

This graph represents the total stages of the sintering.

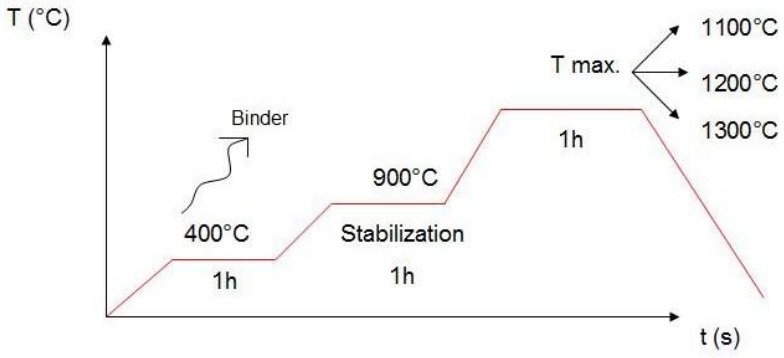


Figure 2.2: Sintering Stages.

To sum up, here are characteristics of the sintering stage.

- ✓ Heating and cooling rate: 200°C/h
- ✓ Atmospheres: Ar-6% H_2 and H_2. Feed: 300 l/h
- ✓ Gas overpressure: 1200-1250 mbar

The sintering procedure follows a heating-cooling rate that could be divided in several parts, as it's shown in Figure 2.2.

First the heating is rising at the rate of 200ºC/h from room temperature until 400ºC is reached. Then the binder used burns out when the sintering stops for 1 hour time. Polymer binders are frequently used when sintering ceramics and they burn out of the ceramic below the sintering temperature.

After the vanishing of the binder the temperature increases again up to 900ºC and it settles there for stabilization one hour. It stabilizes there from the huge temperature gradient it was subjected. Right after one hour the temperature begins to increase again and this time will reach one of the temperatures mentioned on the table above. For Ar-6% H_2 atmospheres it will get up to 1100, 1200 and 1300ºC and for N_2 atmospheres it will reach just 1200ºC for 1 hour both. That is supposed to be the maximum temperature the powders will ever achieve in the sintering stage. After staying in those certain temperatures for it will begin to cool down on a rate of 200ºC/h speed.

Here is a summary regarding all the granules of Cr_2O_3 powders with different compositions of %YSZ with both of the atmospheres and different sintering conditions.

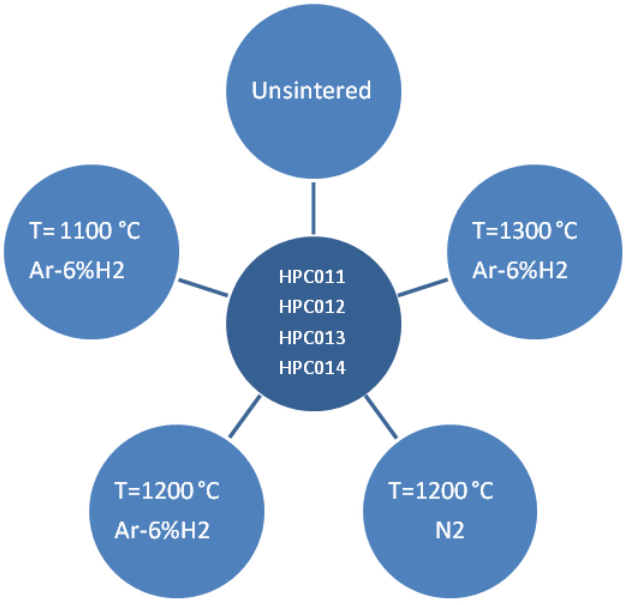


Figure 2.4: Schematic drawing of the sintering conditions of the powders.

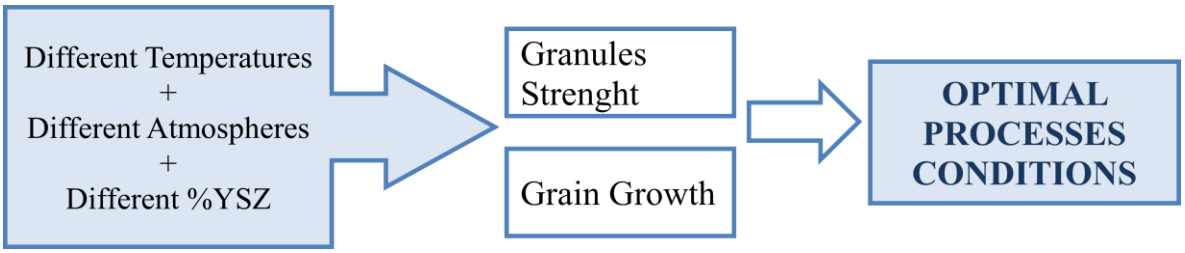


Figure 2.4: Schematic route to develop the optimal processes conditions.

2.2.2. Agglomerate strength tests

The device shown in Figure 2.3 was designed to test the strength of the obtained agglomerates. A total amount of 4gr of powder will be place in the empty die cavity of radius "r". Then an upper punch will press the powders beginning with a residual force of 1N. The sample is pressed at 1mm/min as a rate of speed.

Pressing is stopped whenever the load reaches certain values to allow changes of height in the sample itself. So it is, when the punch making the effort drops down from its original altitude. There is where the breakpoint will occur. The parameters of the test were:

- Load: 0-3.3 kN
- Velocity: 1 mm/min
- Pressure: 0-10 MPa

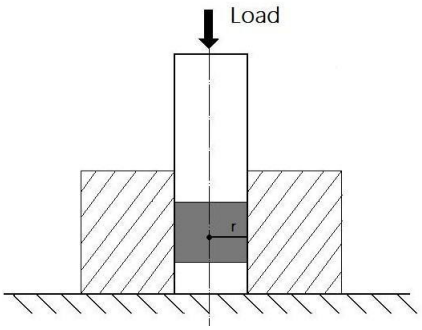


Figure 2.5: *A* die pressing the powders for the estimation of the agglomerate strength

The device works with a rate of:

- Theoretical Maximum: 3.3 kN
- Experimental Maximum: 3.14 kN

Taking into account the radius of the die "r" the area of the die cavity can now be calculated.

- r(die) = 10mm
- Area = $\pi \cdot r^2$ = 314 mm^2

The strength, S(MPa), now can be deliberated when measuring the values of the fore, F(kN).

The agglomerate strength test was developed in a Universal Testing Machine MTS 810. With an error of < 1% and its first recordable force of F = 0.001kN.

Breakpoints are the pressure values at which the agglomerate particles break down. Each of the different powders we mixed previously will be test experimented and analyzed their breakpoints and it will have a significant dependence of the sintering temperature and quantity of YSZ used.

2.2.3. Diagrams and breakpoints

Agglomerate strength tests are used to characterize the strength of material granules. When compaction data are plotted as relative density of the compact (in this case with displacement) versus the compaction pressure, two linear regions are generally observed. The intersection of these regions, which is known as the "breakpoint," has been used as a semi-quantitative measure of agglomerate strength. Comparisons were made between agglomerate breakpoints with several samples tested (Figure 2.4).[15]

Once the *green body* has been broken apart the values of the pressure applied are measured. In addition to agglomerate tensile strength, the mean agglomerate size, the interior macropore structure of agglomerates, as well as the packing efficiencies between and inside agglomerates can be estimated by the procedure.

A straight measurement of agglomerate strength has been so far reported using a single agglomerate strength tester, or microstrength tester, or a nanoidenter. In these devices, spherical agglomerate with known diameter is compressed between two platens and the load-deformation curve is recorded for fracture strength calculation.

Uniaxial die pressing has been used extensively to investigate the relationship between pressure and density variation of powders.

An attempt is made here to estimate agglomerate strength for the experimental measurements of the ***critical nominal pressure*** (Pc) together with the packing efficiency of agglomerate assemblies so as to create a simple method for estimation of agglomerate strength of ceramic powders. Although the test is a useful empirical tool in its own right, the assumption on an average agglomerate strength allows it to guide materials selection and powder manufacturing process variables.

However, compaction of agglomerates happens in three steps generally:

1) Particle rearrangement and sliding without fracture
2) Local deformation and fracture of particles
3) Rearrangement of particles or fracture fragments within granules

There are also components of each during the entire compaction process. When information from a compaction test is plotted as relative density or displacement vs. log compaction pressure, the data frequently show individual linear patterns as shown schematically in Figure 2.4 and 2.5.[16]

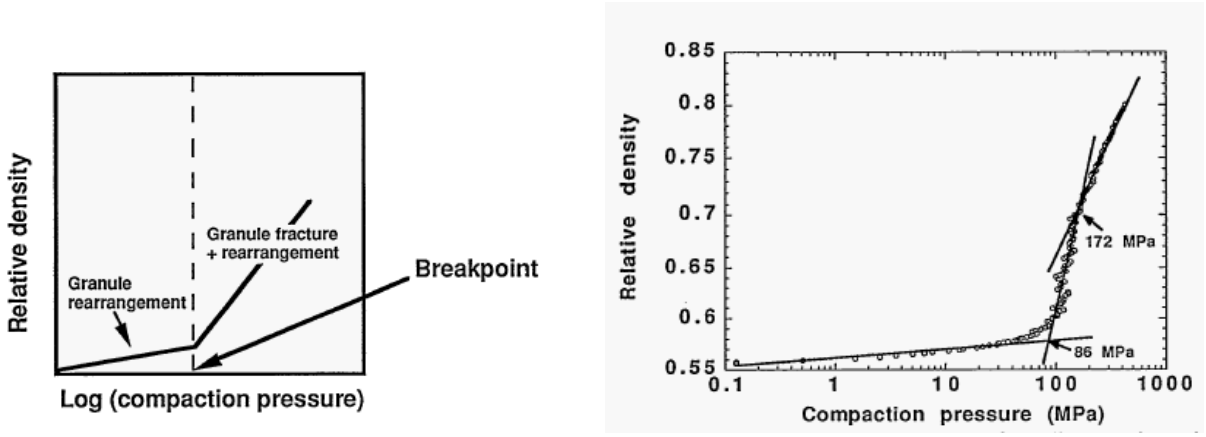


Figure 2.6:Left: Relative Density- Log (compaction pressure) graph. Right: Compaction behaviour. Three linear regions and two breakpoints are observed

Tests with double breakpoint could mean two different ways of compression. Whether the powders are not homogeneously mixed and there are still some air gaps inside the already pressed powders. Or the compressed powders first commit a breakage due to chaotic position and they rearrange again so a second breakpoint can be reached. Beyond this stage agglomerates are locked in their position by mutual contacts and internal friction. The contact forces become more uniform at this stage because of the profusion chains.

If the regular array is accompanied by a distribution in agglomerate strength then the critical nominal pressure (Pc) will be less clearly defined and a curvature of the vicinity of Pc will develop in the die compaction plot. In practice, a regular array does not prevail and there is a distribution in agglomerate size. Thus some rearrangement may also take place in the vicinity of Pc and contribute to the curvature. Contact flattening will go together with rearrangement wherever the free rotation of agglomerates is impeded by friction. This rearrangement may increase the area fraction, used for strength measurement.

Diagrams are constructed from every data from the MTS machine. Axis “x” represents the pressure σ(MPa) going over the agglomerates surface. Those values come up from the force F(kN) data and the already calculated area A(mm^2)

$$\sigma = \frac{F}{A}$$

Axis “y” represents displacement “u (mm)”, the difference between the original height of the sample and the following measures of the next changing heights.

$$u\ (\text{mm}) = \Delta L = L - L_0$$

It also can be represented as *u*(%) or ε(%), parts per unit, Figure 2.6, as the ratio between displacement (mm) and original length (mm). Relative Density (%) is then:

$$\epsilon_e = \frac{l - l_0}{l_0}$$

However, the location of the breakpoint should be the same and the pressure (MPa) related to that point will have the same value.[17]

2.3.Grain Growth Control: sintering effects on the nanostructured samples

Control and optimization of the microstructure is one of the main concerns in the field of advanced ceramics as many significant product characteristics such as mechanical, electrical and optical properties are determined by the final microstructure. Parameters that influence the microstructure of sintered materials are powder characteristics, particle packing and consolidation in green compact, pore structure of green compact, heating rate and sintering cycle. In order to obtain the required final properties, it is important to understand the effects of green microstructure and sintering cycle on densification kinetics and evolution of pore and grain size distributions.

One of the main concerns about the use of nanopowders thermal spray coatings at high temperatures is their stability in relation to sintering effects. Sintering effects may harden and stiffen agglomerates causing an early failure. It has to be observed the effects of high temperatures on the nanostructured regions of nano. [18]

Optimization of a sintering cycle is essentially planned to be at achieving zero porosity (fully dense compact) with minimum possible grain growth.[19]

SEM analysis

Over 300 SEM pictures of the different powders (with diverse sintering temperatures and percentage of YSZ) were taken and measured at magnifications such 1K, 10K, 20K, 250 and 2.5K.

In the Chapter 3 it can be noticed how the agglomerates consist of the grouping of grains joint together. Those grains are all spherically linked together so the ultimate shape can be whether an entire sphere already built up or a circumference in a filling state.

It was decided to focus on 10K and 20K-times amplification pictures to determine two different factors:

1) Grain Size Distribution: from minimum to maximum diameters in every picture.
2) Majority: average of the most common grain sizes.

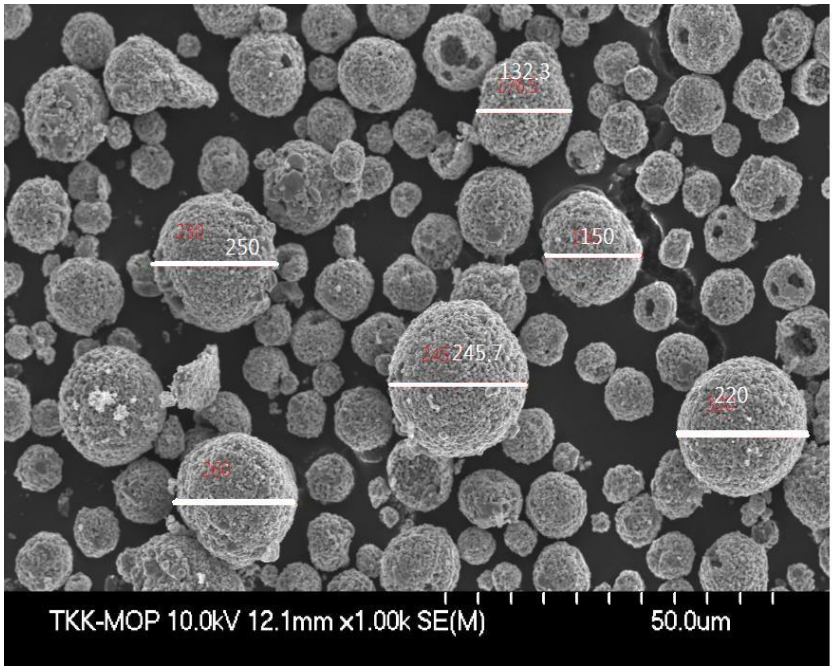


Figure 2.7: Measure taken to HPC0123 at 10K. Maximum grain sizes

3. Results and Discussions

3.1.Strength of Granules

A big problem in the fabrication of ceramic components form fine ceramic powders is the complexity of breaking down or removing agglomerates. Residual agglomerates are claimed to provide strength-limiting failings in sintered ceramics as a result of differential shrinkage or persisting porosity. In plastic forming operations, if agglomerates can be broken down by intensive shearing of the ceramic powder and a binder mixture, the strength mixture of the sintered product can be enhanced. If solid bridges are formed between particles, the resulting agglomerate strength can be very high.

In this work, agglomerate strength tests are used to characterize the strength of material granules. The benefit of the estimation of the agglomerate strength is detecting the ***critical nominal pressure Pc***, a "break point pressure". At pressures lower than Pc, only a very small change in relative density takes place but it increases linearly with the logarithm of the applied pressure when Pc is exceeded. The critical nominal pressure is clearly an indication of an agglomerate strength. Figure 3.1 shows an example of the calculation of P_c.

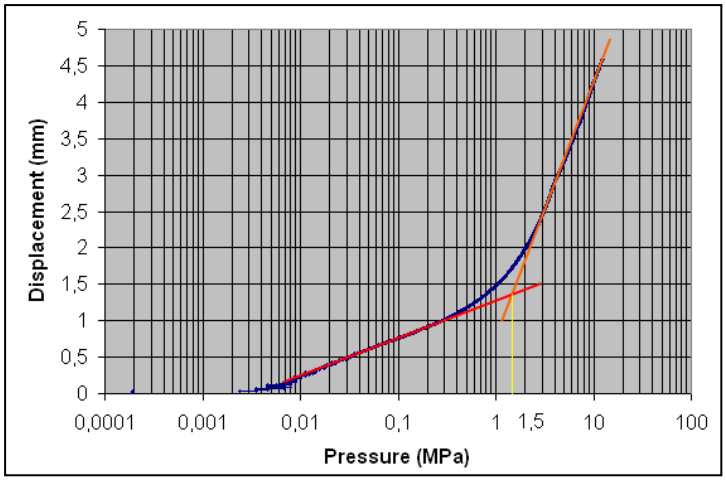


Figure 3.1: Example of Pc for Cr2O3 + 50%YSZ sample.

There are also many sintered granules with different behaviour, i.e. with a double breakpoint (Figure 3.2)

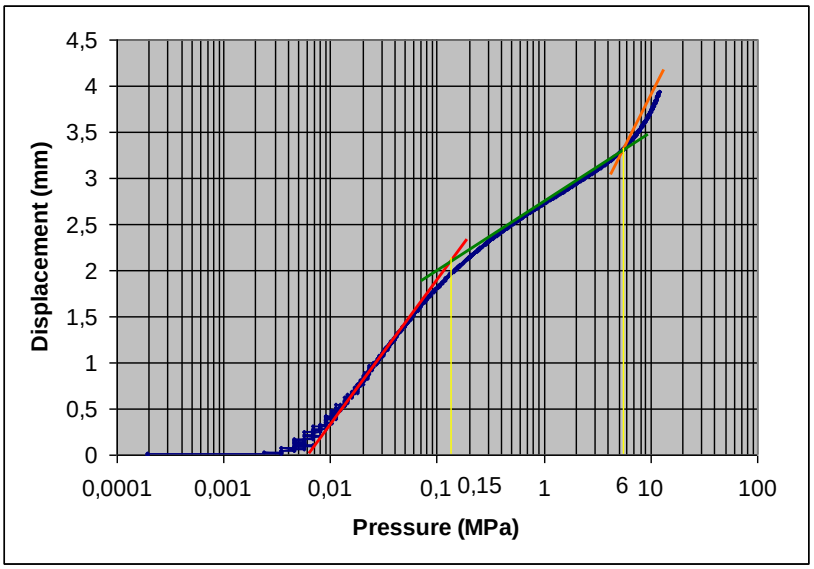


Figure 3.2: Example of HPC013 (1100ºC, Ar-6%H2 sintered) with double breakpoint.

Table 3.1.summarizes the agglomerate strength of materials granulated, depending on composition, sintering temperature and sintering atmosphere.

Atmosphere	T_{sinter} (ºC)	YSZ addition (%vol)	Strength (MPa)	
			1st Breakpoint	2nd Breakpoint
Ar-6%H2	**1100**	-	0,15	5
	1200	-	0,55	5
	1300	-	0,7	1,1
N2	**1200**	-	0,1	5
Ar-6%H2	**1100**	5	0,15	5
	1200	5	0,3	4,5
	1300	5	0,35	
N2	**1200**	5	0,1	6
Ar-6%H2	**1100**	15	0,1	6
	1200	15	0,2	5
	1300	15	0,3	
N2	**1200**	15	0,2	6
Ar-6%H2	**1100**	50	0,15	6
	1200	50	0,4	8
	1300	50	0,2	1
N2	**1200**	50	0,3	7,5

Table 3.1: Strength of granules. *The strength of Cr_2O_3 before sintering is 1.5 MPa*.

The non-sintered granules that only count with one breakpoint, flow better between themselves and there is no rearrangement on them. Instead a constant value for the breakpoints is always achieved, 1.5MPa.

As it was shown in the results from Table 3.1 and from figures 3.1 and 3.2 most of the agglomerates achieved a double point when performing the breakpoint strength test. These happenings affects in all the sintered powders, also in two sintered at 1300ºC. In that first breakpoint it occurs that the agglomerates pass from being single 'compressed powders' to being crushed among themselves and subsequently release all the air in the voids in order to fit in a smaller space. There is an arrangement of the granules. That is why in strengths between 0.1MPa and 0.3MPa there is an inflexion point and later it will happen the breakpoint which determinates the strength of the agglomerates.

The agglomerates sintered at 1300ºC show quite a low values. In some of them a rearrangement on insignificant values is needed and then the real breakpoint is accomplished also with poor results. Sizes of the granules at such high temperature involve a lack of space for them to be able to move and very low ranges of strength to break them when being compressed in the test.

i. Breakpoints vs %YSZ

To underline the effect of YSZ additions, the results are plotted considering the sinter atmosphere. The best way to compare all the percentages of YSZ8 is dividing the samples in the ones sintered in Ar-6%H_2 and N_2. In Figure 3.1 is shown the results of those samples sintered under Ar-6H_2 mixture. We can see that results strongly depend on sintering temperature. When sintering at 1110ºC, increasing de amount of YSZ results in an improvement of properties, more difficult to break, more compact. For higher sintering T, at 1200ºC with 50% YSZ additions, a improvement is achieved. At this T, although the grain sizes have been enlarged after sintering, a liquid phase has been promoted, and lead to a rearrangement of the powders. This produces a more dense granule (agglomerate) and therefore harder to break.

When sintering at 1300ºC, the best result is achieved with those granules free-YSZ. At 1300ºC with no YSZ the agglomerates are mostly a bunch of powders mechanically joint together. In Table 3.3 below, it shown how the granules are linked together as a sphere in the one with no YSZ and the one with 50%YSZ, for example, is linked as spiral of granules due to the liquid phase. A greater densification is shaped with no addition of YSZ.

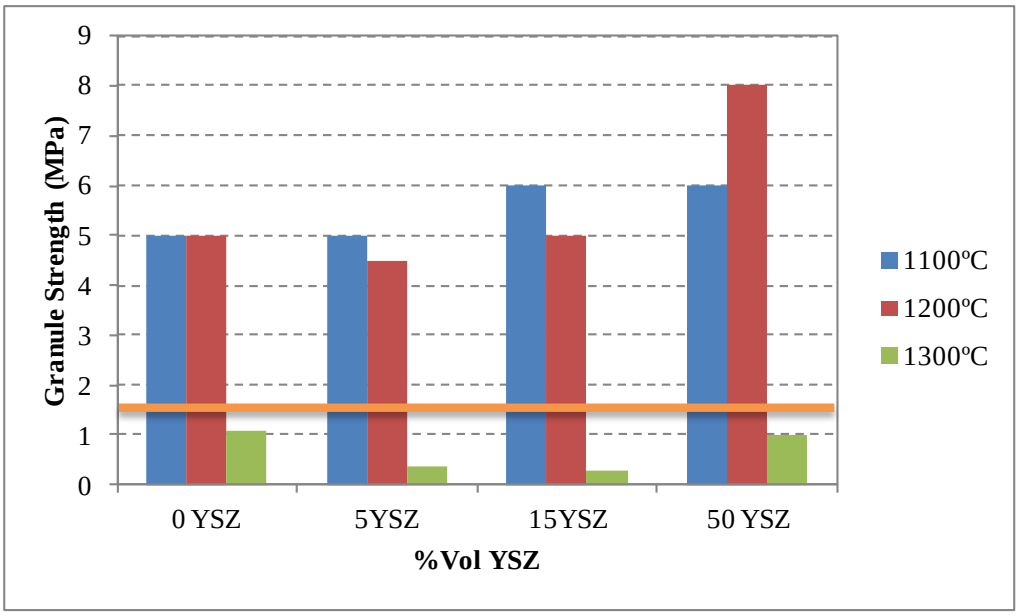


Figure 3.1: Effect of YSZ additions when the sintering atmosphere is Ar-6H_2. Strength of Cr_2O_3 before sintering1.5 MPa

The drop down of Pc values when granules were sintered at 1300ºC will be discussed considering how the grain size in the agglomerates get significantly bigger than the ones sintered at lower temperatures.

Figure 3.2 is focused on 1200ºC and just N_2. In this case, by increasing the YSZ content, PC values increases.

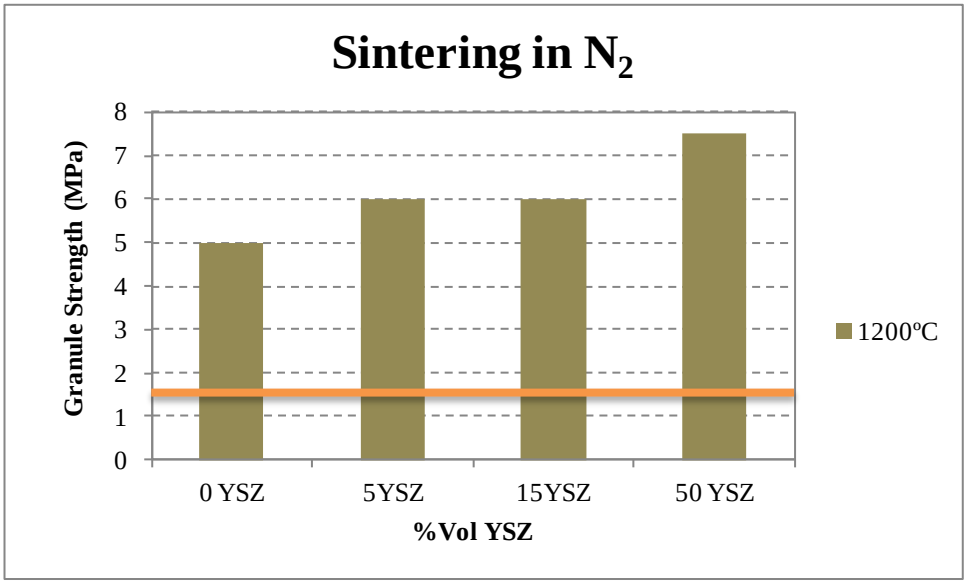


Figure 3.2: Breakpoints according to %YSZ when sintered in N2 at 1200ºC.

ii. Breakpoints vs Atmosphere

Now we check how the sintering conditions also control the maximum pressure values.

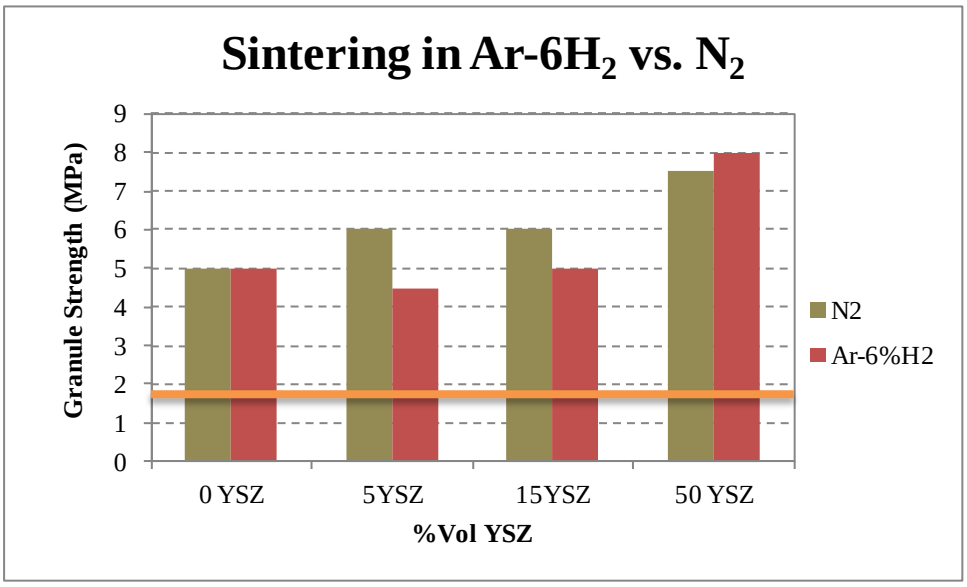


Figure 3.3: Graphic of breakpoints according to their sintering atmospheres and temperatures

The only point of Ar-H_2 higher than N_2 is when the sample has 50% YSZ additions. However the difference is so small (from 7.5 to 8MPa) that we could verify that N_2 represents the atmosphere with the higher strength.

When we considered the microstructure evolution of granules with sintering conditions, we will see how the atmosphere Ar-6%H_2 get the grains bigger than the other atmosphere N_2 which would be a reasonable explanation of why the breakpoints of the samples in Ar-6%H_2 reach lower values than the ones sintered with N_2. The **tendency** as in the breakpoints as in the grain size distributions (shown in the next graphics) shows us greater dimensions of the grains with the Ar-H_2 atmosphere and therefore the granules are less strong compared with the one sintered in N_2 atmosphere.

As it was said previously a N_2 atmosphere is at least 6 times cheaper than the one with Ar-6%H_2, which a wiser use of N_2 could mean a significant cheaper sintering process.

3.2.Grain Size Distribution

After sintering conditions, powders subjected to different temperatures in both atmospheres were pictured and analyzed graphically

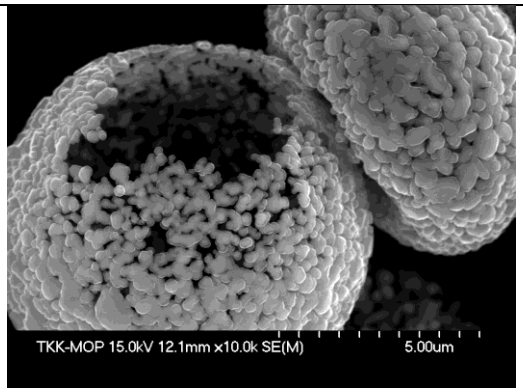
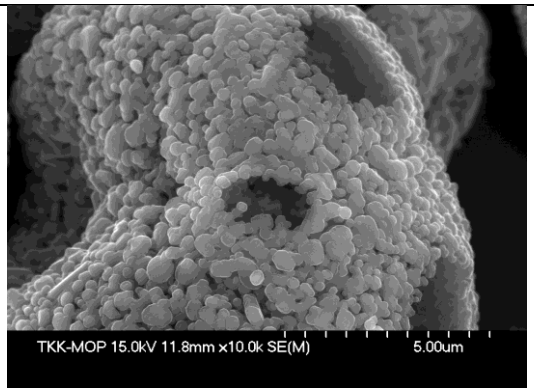
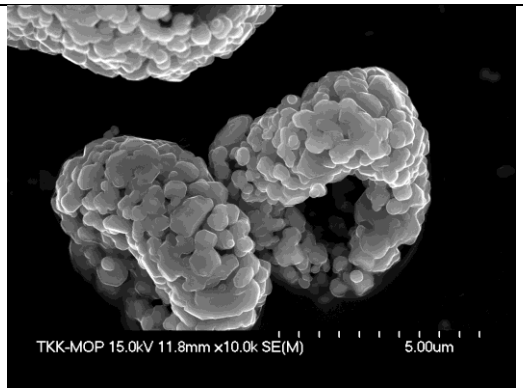
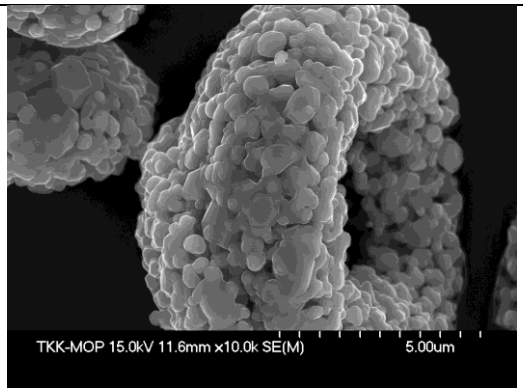
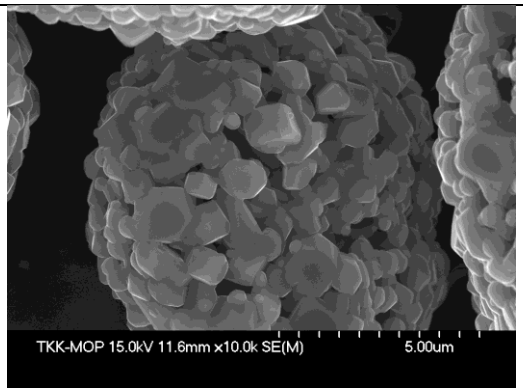
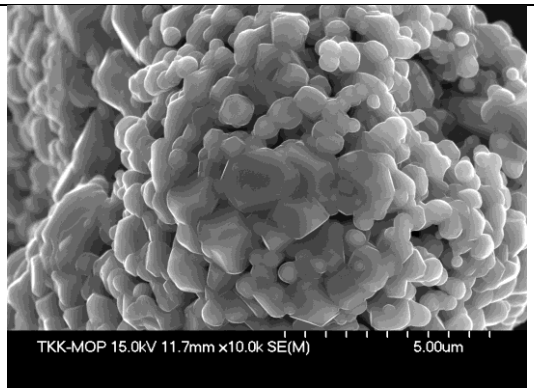
Ar-6%H_2	**Cr_2O_3 + 5%YSZ**	**Cr_2O_3 + 15%YSZ**
1100ºC		
1200ºC		
1300ºC		

Table 3.2: SEM pictures of Cr_2O_3 with the addition of 5 and 15%YSZ shown their evolution with different temperatures

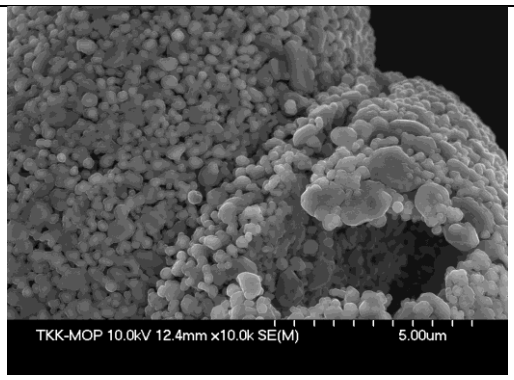
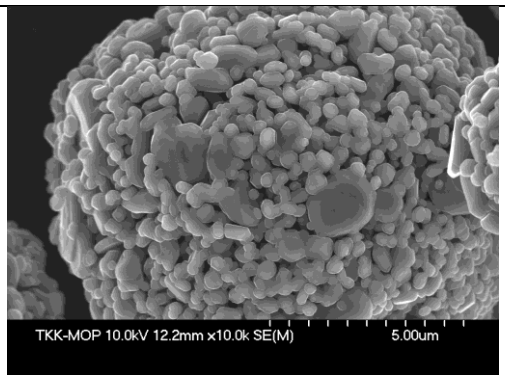
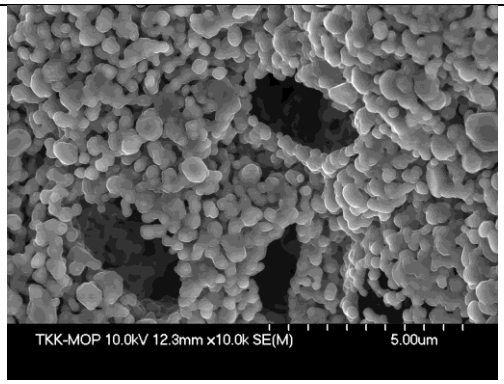
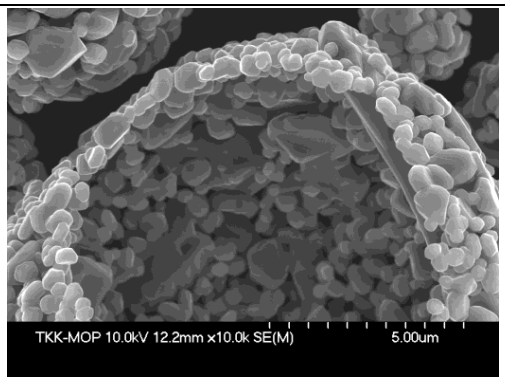
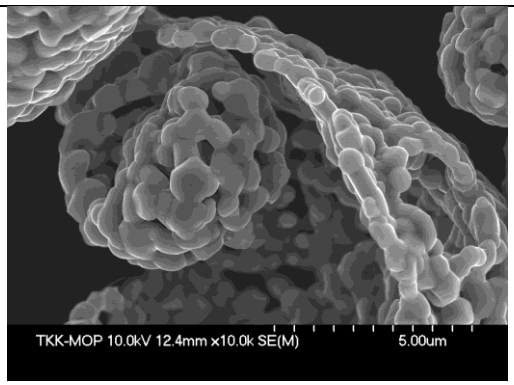
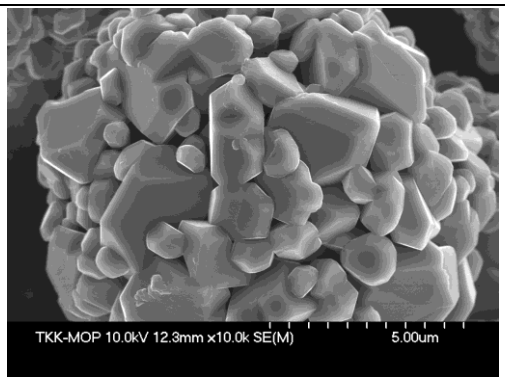
Ar-6%H_2	Cr_2O_3 + 50%YSZ	Cr_2O_3
1100ºC		
1200ºC		
1300ºC		

Table 3.3: SEM pictures of Cr_2O_3 with the addition of 50% and 0%YSZ shown their evolution with different temperatures

It is easily identifiable seeing how the grains grow as long as the temperature increases by comparing pictures with the same magnification (x10k). The agglomerates are joint with less grains as the temperature increases, the same 'spheres' look filled by bigger grains with less amount of them.

The agglomerates used to make these coatings exhibit an individual nanosized Cr_2O_3-YSZ8 particles in Ar-6%H_2, with diameters ranging from 200-400 nm. After 1 h at a temperature from

1100-1300ºC the individual nanostructured granules reached diameters of the order of 400-800 nm, depending of the temperature.[19]

Reviewing the samples that went through the sintering with N_2 atmosphere it will be found the same behaviour.

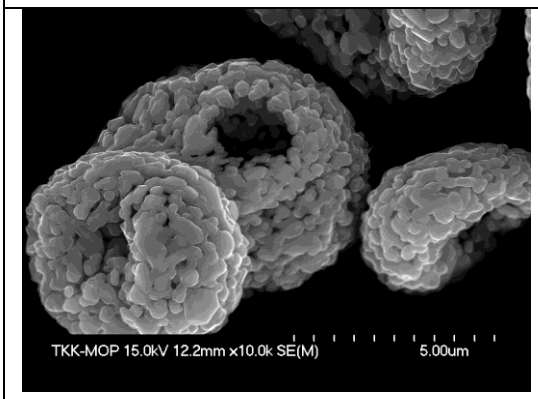
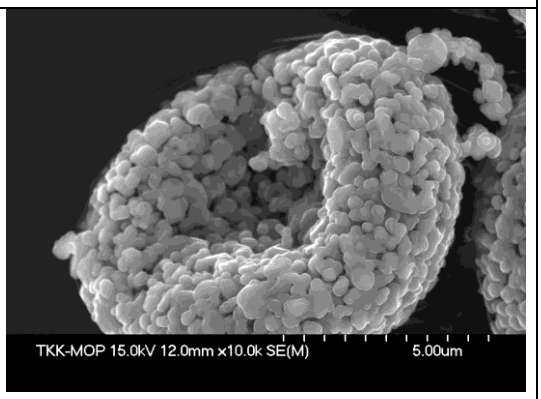
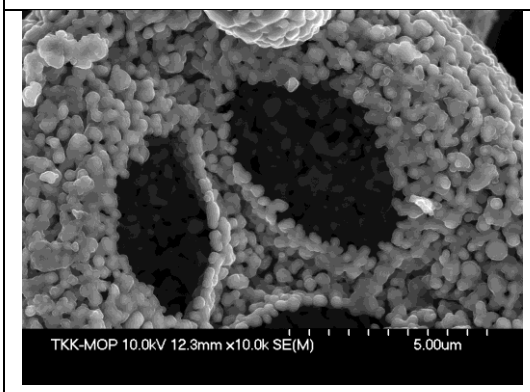
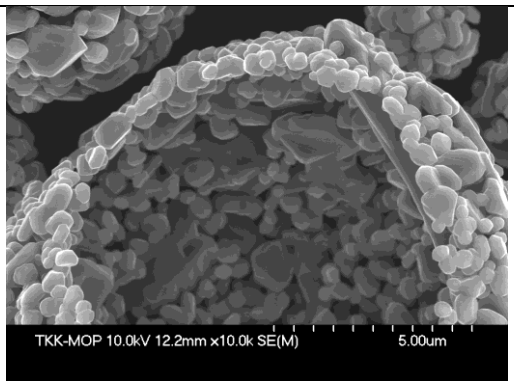
1200ºC N2	**Cr_2O_3 + 5%YSZ**	**Cr_2O_3 + 15%YSZ**
		
	Cr_2O_3 + 50%YSZ	**Cr_2O_3**
		

Table 3.4: Table with all the samples but subjected to a sintering atmosphere of N_2.

The Table 3.4 shows how the percentage of YSZ influences the grain growth of the granules when sintered at the same temperature (1200ºC) in pure N_2. There is also a slight tendency of enlargement in the granules when decreasing the amount of YSZ.

It is frequently suggested that the existence of yttrium in *chromia former alloys* change the growth mechanism of Cr_20_3 scales from one involving principal cation diffusion, to one involving major anion diffusion due to the segregation of yttrium to the grain boundaries, as it was mention in the *1.4.1.2 Coatings for Corrosion Protection*. It is also suggested that the presence of yttrium can form Cr_20_3 scales which act as a better diffusion barrier. [20]

It is perfectly shown how the amount of YSZ influences the grain size after sintering. The more additive has the less the grains grow during sintering. In the ones from 50%YSZ it can be seen that the grains remain small while in free-YSZ granules, the enlargement of the grains is clear and visible.

The next table, Table 3.3, demonstrates how the grain distribution and the grain average are a clear consequence of the temperature and the percentage of additive on the nanopowders. Measuring the majority diameters of the grains we can see an intuitive statistic of development of the grains.

Atmosphere	T_{sinter}	YSZ addition (%vol)	Grain size distribution (nm)	Majority (nm)
Ar-6%H2	**1100**	0	200-900 (10K)	300-500 (10K)
			200-600 (20k)	300-400 (20k)
	1200	0	300-900 (10K)	300-700 (10K)
			200-700 (20k)	300-500 (20k)
	1300	0	200-2000 (10K)	400-1500 (10K)
			700-1700 (20k)	800-1100 (20k)
N2	**1200**	0	200-1000 (10K)	200-500 (10K)
			100-600 (20k)	300-500 (20k)
Ar-6%H2	**1100**	5	100-1000 (10k)	250-350 (10k)
			100-700 (20k)	250-350 (20k)
	1200	5	100-1500 (10k)	400-600 (10k)
			150-1000 (20k)	400-500 (20k)
	1300	5	250-2000 (10k)	800 (10k)
			150-2500(20k)	500-700 (20k)
N2	**1200**	5	100-800 (10k)	500 (10k)
			100-1600 (20k)	300-400 (20k)
Ar-6%H2	**1100**	15	100-800 (10k)	300-500 (10k)
			100-500 (20k)	200-300 (20k)
	1200	15	300-900 (10k)	500-700 (10k)
			200-600 (20k)	200-400(20k)
	1300	15	400-900 (10k)	600-900 (10k)
			200-900 (20k)	400-500 (20k)
N2	**1200**	15	200-1000 (10k)	600-700 (10k)
			300-1000 (20k)	400-700 (20k)
Ar-6%H2	**1100**	50	200-500 (10k)	200-400 (10k)
			200-400 (20k)	300-400 (20k)
	1200	50	300-800 (10k)	500-700 (10k)
			200-600 (20k)	200-400 (20k)
	1300	50	300-1000 (10k)	500-800 (10k)
			400-700 (20k)	200-500 (20k)
N2	**1200**	50	200-600 (10k)	200-400 (10k)
			200-500 (20k)	300-400 (20k)

Tabla 3.5: Grain Size Distribution by average and Maximum and Minimum sizes determined by each magnification.

Material	Grain size distribution (nm)	Majority (nm)
Cr2O3	100-700 (10k)	100-300 (10K)
	100-500 (20k)	200-400 (20k)
Cr2O3+5%YSZ	100-600 (10k)	200-300 (10k)
	100-600 (20k)	200-400 (20k)
Cr2O3+15%YSZ	100-500 (10k)	200-300 (10k)
	200-500 (20k)	300 (20k)
Cr2O3+50%YSZ	100-400 (10k)	200-300 (10k)
	200-400 (20k)	200-400 (20k)

Tabla 3.6: Grain Size Distribution of Cr2O3 un-sintered powders.

Here we have a notion of how the grains changes from maximum to minimum sizes depending the temperature they experiment at 10K magnification according with the previous Table 3.5.

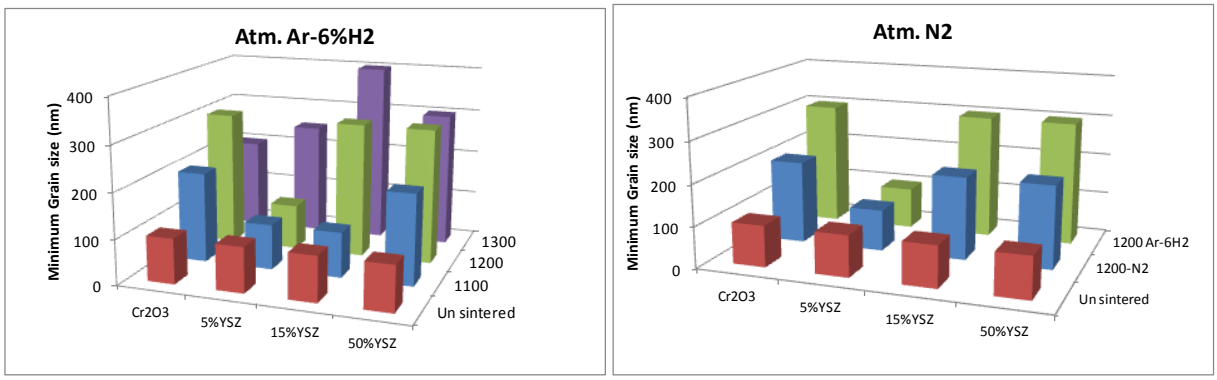


Figure 3.4: Grain size distribution at 10k: Minimum size of the granules.

The tendency of the powders is to grow according with the raise of temperature. It is obvious that the unsintered agglomarates remain with an average size of 250nm, as it says in Figure 3.6. However there is a significant raise of the grain size at 1200ºC where the dimensions are over 30% more than the previous ones. There is a big shrinkage in temperatures below 1200ºC and after that the volume begins to increase over 1200ºC due to the formation of the liquid phase during sintering.[21]

Comparing the same temperature, N_2 sintering atmosphere provides conditions that have been limited the particle growth of these granules.

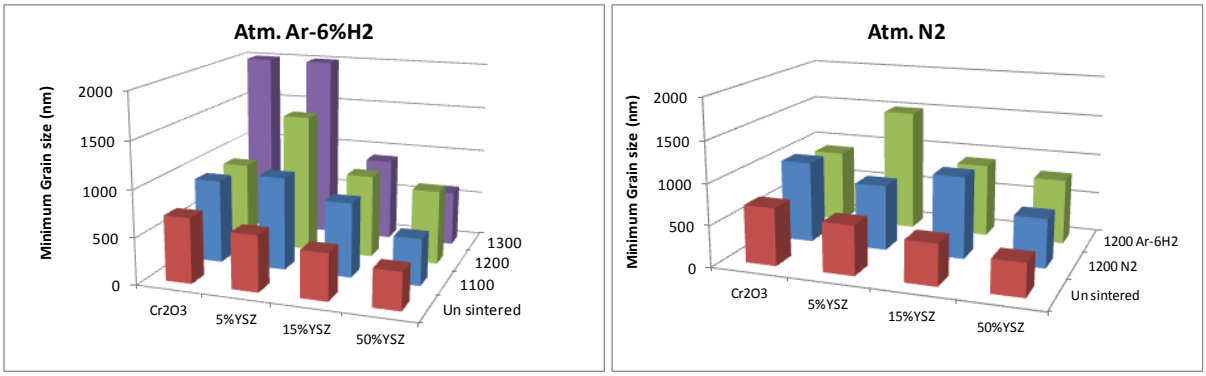


Figure 3.5: Grain Size distribution at 10k: Maximum size of the granules

It is easily seen how grain sizes increase with the temperature for minimum and maximum grain sizes, from un-sintered specimens to as-sintered at 1300ºC. Nevertheless when the minimum sizes of the granules barely reach 350nm the maximum magnitudes taken when measuring the largest granules achieve an average of 1200nm.

To understand better the evolution of grain growth depending on specimens, it has been considered the average of the majority grain size (figure 3.6).

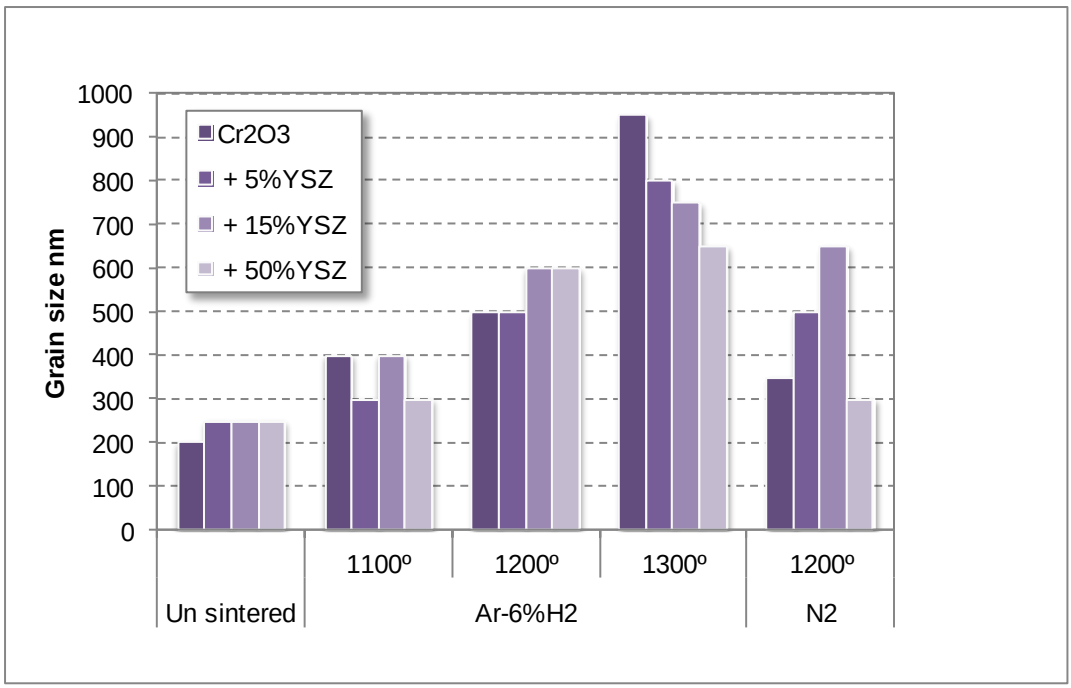


Figure 3.6: Relation between grain size averages (majority) with the sintering temperature at 10K.

Again, there is the affinity of the grain growth to increase with the temperature, as expected and the comparison with the non-sintered powders remaining with an average size of 250nm.

Influence of YSZ composition depends on sintering temperature. At 1100ºC, there is not a clear correlation; grain size seems to be governed by thermal activation more than for sintered aid.

By increasing sintering temperature, at 1300ºC the addition of YSZ is critical to control and to reduce the final grain size, ie., to avoid grain coarsening.

It is remarkable, the result achieve in N_2 for 50%YSZ addition, which attains the lowest grain size.

i. Grain Size vs Granule strength

Grain size strongly affects when sintering is done at 1300ºC. The coarsening phenomena, reduce the granule strength below 1MPa (fig 3.7).

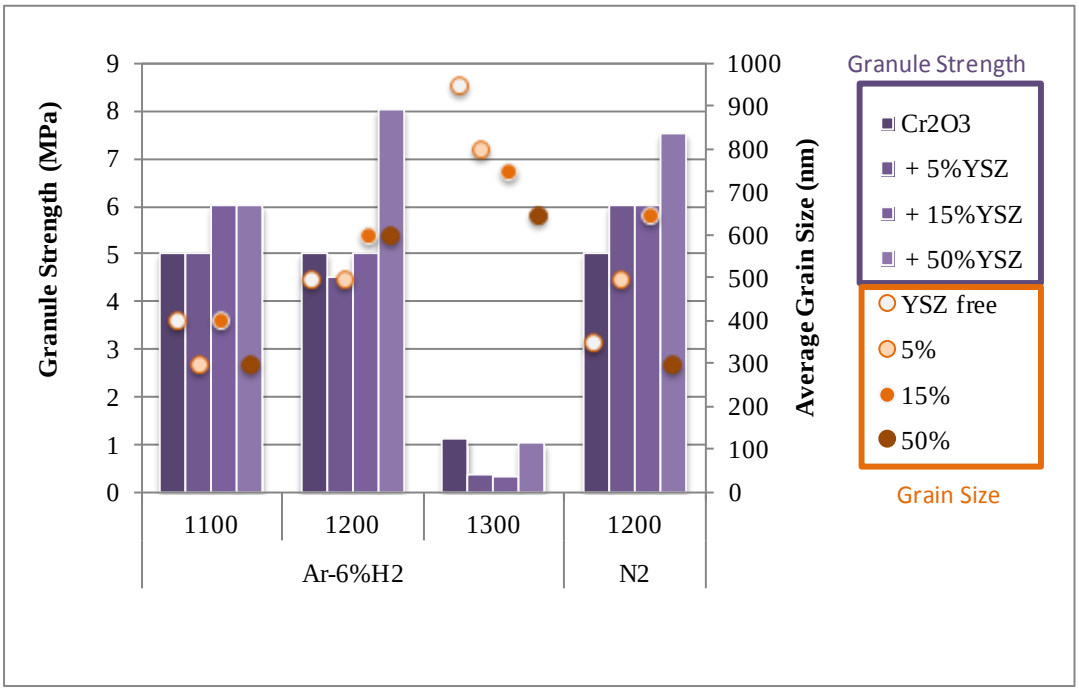


Figure 3.7: Grain Size vs Breakpoints

In conclusion, the goals to achieve are mostly minimum grain size on the granules and maximum granule strength. However, a cheap atmosphere and the lowest temperature when sintering will contribute to have also a reasonable manufacturing in the future, when the optimum conditions are chosen

.

4. Conclusions

It has been reached the main aim of this Master Thesis. The goal was to develop new ceramic coating material to be able to be effectively sprayed with HVOF based on the improvement of improving particle strength, controlling the grain growth and therefore optimizing the sintering parameters applied to obtain the granules that feed the HVOF system.

Considering the granule strength

At studying breakpoint values regarding the amount of %YSZ we can clearly see how much influences the quantity of sintering aid to Cr_2O_3. Therefore, the more Cr_2O_3 contains YSZ8 the more strength the powder becomes. Even dividing both atmospheres the behavior of the pressure points works the same way for Ar/H_2 and N_2 and when looking at simple chromia it can be seen the lowest points easily.

When checking breakpoints influenced by their sintering conditions it has been learnt mostly that un-sintered powders have really poor mechanical properties compared to the sintered ones. Also the samples sintered at 1300ºC had irregular poor pressure values as well. From 1100ºC to 1200ºC powders get stronger and there is a tiny tendency of acquiring more stiffness when the graph jumps from 1100ºC to 1200ºC. Although uncertainly it can even be said that N_2 in 1200ºC achieves the best result.

So far relating atmospheres, it's being learnt that N_2 obtains the best outcomes, although both atmospheres flow quite at the same level, N_2 seems to accomplish better rates at the unique temperature tested with it.

Considering the grain growth of granules

When focusing at grain sizes it can be seen a significant rise of the grain growth from 1100ºC to 1300ºC. Plain chromia grew the most and the powders mixed with YSZ addition were decreasing respectively from 5% to 50%YSZ. Again samples sintered in N_2 reached better values and simple Cr_2O_3 got the lowest pressure values. However, all the processed granules fulfill the features and conditions for feeding the equipment for HVOF.

Summing up and concluding:

1. Temperatures below 1300ºC seem to be suitable enough for obtaining small grain sizes, essential to have good mechanical properties.
    - Furthermore, when temperature raises the average price generally tends to enhance.

2. There is not much difference among breakpoint results, over the range 1100ºC and 1200ºC, in order to have good parameters for sintering. It may mean:
    - Both atmospheres are good enough to achieve the same results. However, in order to take a decision:
        a) N_2 is considerably cheaper then Ar/H_2
        b) N_2 always seem to bring powders more strength than $Ar\text{-}6\%H_2$.

3. Higher quantities of YSZ reach better breakpoint results, but it has to be considered than YSZ is more expensive than Cr_2O_3.

4. Parameters such 1100°C in Ar/H_2 are good enough to achieve good quality results. Nevertheless 1200°C N_2 has also quite accurate results as well.

<u>CONSIDERATIONS FOR FUTURE WORK</u>:

- ❖ It should to be tested 1100°C N_2 to see if it is possible decrease the temperature and obtain the same effects.
- ❖ Different percentages of %YSZ between 15% and 50% has to be a must in order to check out if there will be lower quantities of YSZ that could achieve similar results to the ones tested.

5. References

[1] Martin, J W. Materials for Engineering. Cambridge, GBR: Woodhead Publishing, Limited, 2006. (http://site.ebrary.com/lib/ttyk/Doc?id=10131830)

[2] **http://www.gordonengland.co.uk/corrosion.htm**

[3] Handbook of thermal spray Technology, ASM international, 2004 (www.asminternational.org*)*

[4] Ref: Lech Pawlowski, "The Science and Engineering of Thermal Spraying Coatings", Great Britain: Wiley, 1995

[5] Ref: HVOF Sulzer Metco data sheets

[6] **http://www.gordonengland.co.uk/corrosion.htm**

[7] Growth mechanism of Cr203 scales: oxygen and chromium diffusion, oxidation kinetics and effect of yttrium. S.C. Tsai a, A.M. Huntz a, C. Dolin b

[8] Lech Pawlowski, "The Science and Engineering of Thermal Spraying Coatings", Great Britain: Wiley, 1995

[9] Ceramic CRC Materials Science and Engineering Handbook

[10] Interfacial Microstructure of Chromium Oxide Coatings. By Xiaolu Pang, Kewei Gao, Huisheng Yang, Lijie Qiao, Yanbin Wang and A. A. Volinsky. Advanced Engineering Materials 2007,9, No. 7

[11] Minh, N.Q. (1993). "Ceramic Fuel-Cells". Journal of the American Ceramic Society American Ceramic Society (29 May 2009). **Progress in Thermal Barrier Coatings** John Wiley and Sons

[12] Nanostructured and conventional YSZ coatings deposited using APS and TTPR techniques. O. Racek a, C.C. Berndt b,., D.N. Guru c, J. Heberlein c (October 2005)

[13] P. Hones, M. Diserens, F. Levy, Surf. Coat. Technol. 1999, 120/121, 277.

[14] Interfacial Microstructure of ChromiumOxide Coatings** By Xiaolu Pang, Kewei Gao,* Huisheng Yang, Lijie Qiao, Yanbin Wang and A. A. Volinsky

[15]A Comparison of Pressure Compaction and Diametral Compression Tests for Determining Granule Strengths. S. Jill Glass and Clay Newton, Sandia National Labs, Albuquerque, NM, 87185

[16]A Comparison of Pressure Compaction and Diametral Compression Tests for Determining Granule Strengths. S. Jill Glass and Clay Newton, Sandia National Labs, Albuquerque, NM, 87185

[17] "A Die Pressing Test for the Estimation of Agglomerate Strength" Jin-Hua Song and Julian R- G-Evans. Department of Materials Technology, Brunel University. United Kingdom.

[18] Thermal Spray Coatings Engineered from Nanostructured Ceramic Agglomerated Powders for Structural, Thermal Barrier and Biomedical Applications: A Review R.S. Lima and B.R. Marpl(Submitted September 15, 2006; in revised from December 7, 2006)

[19] Computer-aided control of the evolution of microstructure during sintering. Manjunath Subbanna, P.C. Kapur, Pradip——————————— Tata Research Development and Design Centre, Pune 411 013, India.

[20] Growth mechanism of Cr203 scales: oxygen and chromium diffusion, oxidation kinetics and effect of yttrium. S.C. Tsai a, A.M. Huntz a, C. Dolin b

[21] Sintering of Cr_2O_3 in H_2/H_2O Gas Mixtures. T. Li*, R. J. Brook and B. Derby. Department of Materials, University of Oxford, Oxford, OX1 3PH, UK